HIGH FIDELITY DETECTION OF DEFECTS IN POLYMER FILMS USING
SURFACE-MODIFIED NANOPARTICLES

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HIGH FIDELITY DETECTION OF DEFECTS IN POLYMER FILMS USING SURFACE-MODIFIED NANOPARTICLES

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Thesis

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ABSTRACT

Several high technology applications, such as the development of Integrated Circuits, require complex layer-by-layer integration of new materials and processing over large areas that rely on techniques such as chemical mechanical planarization (CMP) to remove material in a planar and uniform fashion. CMP is an example of a process controlled by various parameters such as slurry concentration, spin speed, pattern density, hardness of the polishing pad, temperature etc. where minor deviation from the set process parameters leads to several critical defects including stress cracking, delaminating at weak interfaces, pitting and corrosive attacks from slurry chemicals. The current method of detection of these defects is scanning electron microscopy (SEM), which on a 12inch Si wafer can take up to 48 hours. Likewise, there are many other large area polymeric coating applications such as pacemakers where pin-hole defects can be critical to performance. The detection of these defects poses a major challenge and is an example of the classic “needle-in-haystack” problem for nano and macroscale detection. We address this issue by developing a novel, efficient method for the optical detection of surface topographical features using fluorescent nanoprobes, which are surface-modified polystyrene nanospheres whose ability to detect surface features can be tuned via size (entropic effects) and chemical properties (enthalpic effects). We have successfully applied this approach to detect numerous types of artificial and natural defects on polymeric and non-polymeric substrates including lines, pinholes and sharp edges. This
method can elucidate the surface structure of large areas in a minimal amount of time. It is estimated that this new method will decrease imaging time compared to traditional imaging methods like atomic force microscopy (AFM) and SEM by 50 fold. Our defect detection approach is particularly applicable to many problems where polymers are used in the form of surface and interfacial layers in hybrid nanomaterial films.
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CHAPTER I

INTRODUCTION

1.1 Introduction to defects in nanoelectronics

Defects are ubiquitous to materials and material surfaces. As we keep pushing thresholds of length scales, producing them defect free is a challenge, while it becomes increasingly difficult to detect their presence over multiple length scales. The perfect example would be the semiconductor industry where the driving force continues to be higher performance and lower cost. With time, transistor size, interconnect wiring dimensions and power supply voltages will decrease steadily while chip speed, transistor count, wiring density and the number of input/output (I/O) circuits will only increase steadily (Pai, Ting, & Oldham, 1988).

An impressive series of process innovations, including chemical mechanical planarization (CMP), have enabled this trend for nearly four decades (Oliver, 2004). At various steps in processing a silicon integrated circuit (IC), surface topography from underlying layers can cause yield-limiting problems for the next process step. CMP has emerged as the premier method for achieving ultra flat surfaces when they are most critical, thus enabling many of the advanced electronic devices currently in production.
As a result of these changes, the process of analyzing failures and the nature of defects that cause them will be transformed (Y. Li, 2008). The current chapter starts with an introduction to the significance of chemical mechanical planarization and the various issues with CMP that eventually lead to defects and failure of the IC. The discussion then addresses failure analysis (FA) and the methods employed for their detection, along with the current state of imaging of defects on the substrates planarized using the CMP process. The goal of this research is to design an effective method for detecting physical, chemical and physico-chemical defects in a novel approach that circumvents imaging sector-by-sector scanning for defects, which is extensively time-consuming. This was achieved through the use of fluorescent nanoparticles. In order to develop the systematic approach to defect detection with nanoparticles, it is essential to understand the inherent nature of interactions between nanoparticles and various substrates, and with defects that may occur on the substrates. The latter part of the chapter deals with understanding these interactions.

1.2 CHEMICAL MECHANICAL PLANARIZATION: SIGNIFICANCE

CMP became a mainstream process at and below the 0.35 µm technology node. The first high-volume processes were oxide CMP for interlevel dielectric (ILD) planarization and tungsten (W) CMP for contacts and vias. Since then the number of materials being polished in various complimentary metal-oxide-semiconductor (CMOS) process flows has steadily grown, as shown in Figure 1.1 (Rhoades, 2008).
A complexity involved with CMP is that each substrate layer generally requires unique slurry, a properly designed polishing pad, optimized process settings for both polish and post-CMP clean, and other factors that must be individually tailored to the application. Successful results are achieved only when all the pieces of the puzzle fit together (Mielli, Barros, Lopes, & Carreño, 2008).

The first widespread application of CMP was the planarization of interlevel dielectric (ILD) oxide layers. The topography resulting from lower levels of patterned films can create a very non-planar ILD surface, which creates severe difficulties for at least three subsequent process steps: photo, metal deposition and metal etch (Stine et al., 1997). The depth of focus (DOF) at photolithography is a direct function of the illumination wavelength and sets an upper limit on surface height variation that can be
accommodated and still maintain crisp feature definition. In order to print smaller features, topography has to be reduced (Y. Li, 2008).

A second problem was poor sidewall step coverage at the next metal deposition. Finally, metal etch required excessive over-etch for complete removal of metal stringers at the bottom inside corners. All three of these factors became virtually impossible to solve with existing techniques at the 0.35 micron technology node; thus oxide CMP was born. The development of tungsten (W) CMP was driven by different factors (Chen, Wang, & Juang, 2007). The basic concept for tungsten contacts, vias or local interconnect is to etch features into an oxide layer, which are then coated by a thin barrier metal and filled with conformal CVD tungsten. Tungsten is removed from the top surface leaving inlaid metal features that are electrically isolated from each other. Unfortunately, CVD W deposition processes are prone to chamber flakes, gas phase nucleation and other sources of particles or defects. Tungsten CMP solved two key issues:

1) Particles, flakes and other defects were mechanically wiped from the surface, and

2) Tops of plugs were left virtually coplanar with the oxide rather than recessed as happened with etch back.

This led to substantial yield improvements and enabled stacked vias in design rules for multilevel interconnect.

The third mainstream CMP process was shallow trench isolation (STI) CMP. In the early steps of IC manufacturing, transistors must be electrically isolated from each
other, which was previously done with a technique known as LocOS (Local Oxidation of Silicon). STI enables transistors to be isolated at much closer spacings thus allowing further design rule shrinks (David et al., 1996). As IC technology evolved toward the 0.25micron node, interconnect delays due to resistance-capacitance (RC) time constants were rapidly becoming the limiting factor for circuit speed rather than transistor gate delay. With only three metals (gold, copper and silver) having lower resistivity than aluminum, choices for lowering R were limited. Copper emerged as the most tractable option even though plasma-based Cu etch failed. Rather than etching lines as had been done for decades with aluminum, patterning of Cu interconnects is done with the dual damascene process (Nishi & Doering, 2007).

To meet planarity requirements for dishing and erosion, most Cu processes are performed in three stages:

1) Bulk planarization stopping just above the barrier layer,

2) Soft landing with high selectivity to barrier, then

3) Barrier removal and final surface finish.

This effectively turns one CMP process into three different processes performed in series (Miyajima, Akaboshi, Yogo, & Kojima, 2000; T. Park, Tugbawa, Boning, & Pan, 1999). The first two stages often use the same slurry (though not necessarily) and require a planarizing pad. The third stage requires different slurry and often a different planarizing pad, which may be chosen for selectivity performance if the barrier slurry is relatively nonselective.
1.2.1 LENGTH SCALES IN CMP PROCESS

Many theoretical models of CMP are based on or derived from a simple equation known as Preston’s Law, which states that removal rate is linearly proportional to the product of pressure and velocity (Y. Li, 2008; Seok, Sukram, Borucki, & Jindal, 2003). This “law” provides a reasonable model for mechanical wear, but is not adequate for CMP. It does not account for chemical effects, such as etching, reaction thresholds, depletion/saturation, temperature sensitivity or electrochemistry (in metals). It also does not account for nonlinear fluid dynamics, particle-surface interactions, tribological effects, time-dependent pad surface wear, pad conditioning, polymer properties, and more. A recurring complexity of CMP is pattern density sensitivity (Ahmadi & Xia, 2001; Kulkarni, Ng, Baker, & Her, 2007; J. Li, Lu, He, & Luo, 2011). Simply stated, pattern density is the fraction of high area to total surface area. For oxide CMP, the underlying metal drives this. For other layers, high may refer to field areas between recessed features. The rate at which high features are removed is proportional to the effective contact pressure, which equals the average pressure divided by the local pattern density. The region considered “local” is a direct function of planarization length, which is roughly the lateral distance required for relaxation of deflections in the pad surface (Chandra, Guha, & Subhash, 2001; J. Li et al., 2011; T. H. Smith, Fang, Boning, Shinn, & Stefani, 1999).

To provide an example of the relative sizes and lengths involved in CMP, Rhodes used a scaled comparison to make it easier to visualize (Rhoades, 2008). According to him, “Imagine a world in which 1 micron is scaled up to 1 inch (2.54 cm). A typical
slurry particle (actual diameter about 100 nm) would be scaled up to 0.1 inches, or roughly the size of a large grain of sand. With this upscale world in mind, it may be easier to understand why CMP is considered a dark art. It is like planarizing an airport with bumps ranging from toothpicks to tool sheds by pressing it against a spinning polymer city flooded with chemical soup.”

(b) 1.2.2 ISSUES WITH CMP

Virtually any CMP module can be described by a series of events.

1. Deposit desired film or film stack onto the device side of wafer
2. Load unprotected wafer into rotating carrier (device side down)
3. Flow slurry (mixture of chemicals and trillions of suspended particles) onto large diameter rotating polymer pad
4. Lower wafer onto pad and apply a controlled pressure ranging from roughly fifty to several hundred pounds
5. Polish until sufficient amount of the film stack has been removed
6. Clean up residue left on wafer surface

One challenge is that interactions between process settings and output metrics are not simple to predict. They are seldom linear and they strongly depend on slurry, smoothening pad, film stack, process recipe settings, and design rules of devices being polished (Kaufman, Coppeta, Racz, Rogers, & Philipossian, 2000; S. H. Li & Miller, 2000). One of the biggest concerns in IC manufacturing is a defect. Over a span of four decades, the industry has spent billions of dollars and thousands of careers battling the forces of defectivity. Slurries have trillions of particles that must be removed before
wafers leave the process bay (Adams, Dornisch, Krulik, & Persichini, 1995). Numerous approaches have been attempted for post-CMP cleaning (Busnaina, Lin, Moumen, Feng, & Taylor, 2002; Y.-L. Wang, Liu, Feng, & Tseng, 1998). The most popular involve immersion in a megasonic bath or double-sided scrubbing with polyvinylacohol (PVA) brushes (Reinhardt & Reidy, 2011; S. R. Roy, 1999), (Philipossian & Mustapha, 2004; Singh, Wargo, & Stockbower, 2007), or both. These processes utilize post-CMP cleaning chemistries formulated for the exposed materials and slurry particle type.

Beyond slurry particles, wafers are vulnerable to other defect mechanisms during CMP. Particle size distribution must be tightly controlled in both manufacturing and slurry handling systems to avoid large agglomerates that can scratch the surface. Chemistries of both slurry and post-CMP clean must be controlled to avoid pitting or surface roughening (Kim et al., 2007; Miranda, Imonigie, & Moll, 2004). Buried defects that were initially not observable can be uncovered during CMP that requires more trouble-shooting. In addition to the general concerns, each CMP process has unique issues. For oxide CMP, the polish begins and ends in the same material, unlike most other CMP processes. This makes repeatability and control important since variations in polish rate or uniformity translate directly into oxide thickness (Grillaert et al., 1999; Shui & Chen, 2008).

Pad conditioning is key to process stability. Proper pad surface texture is required for optimal removal rate and uniformity, but establishing this texture once at the beginning of pad life is not sufficient. Each cycle tends to wear down the high points
(called pad asperities), and polishing by-products tend to form a “glazing layer” on the pad. Pad conditioning counteracts both of these effects, but overly aggressive conditioning cuts away more pad than necessary and artificially shortens pad life (Shui & Chen, 2008). Tungsten CMP generally runs at relatively aggressive settings (Yang et al., 2007). This leads to high pad surface temperatures and associated thermal gradients that may contribute to process instability (Ollendorf, Cabral, & Fuller, 2004). Basic terms and failure modes associated with Cu CMP are shown in Figure 1.2.

![Copper CMP Terminology](image)

Figure 1.2 Cu CMP Terms and Common Failure Modes

Failure mechanisms on device structures include erosion and plug coring. Erosion is array thinning of densely spaced plugs due to mechanical wear of the oxide stop layer (Jung et al., 2001). Coring is a term used to describe undesired etching of weak plug centers by slurry chemistry, which can lead to high contact resistance or electrical opens affecting both yield and potentially reliability of finished devices. STI CMP is similar to
oxide CMP in that silicon dioxide is the primary material being polished, but with very different performance requirements (Duane Boning & Lee, 2002).

Successful completion of the STI module requires that CMP fully remove oxide over all nitride features (active areas) without breaking through nitride anywhere. With nitride layers typically only a few hundred Angstroms, this is a significant challenge, especially if attempted with traditional oxide slurries with only about 3-to-1 selectivity. Pattern density variation renders this approach nearly impossible if small isolated features and large or dense structures exist in the same die. The preferred solution today is slurries specifically formulated with extremely high selectivity to nitride (Liang-Yong et al., 2011; Yoon et al., 2002).

Copper CMP is the last mainstream process to be considered and is arguably the most complex. Cu is highly reactive and has a tendency to scratch, corrode, etch or form a galvanic cell with other metals in many aqueous chemistries. From beginning to end of the polish sequence, the surface goes from being 100 percent Cu to a blend of two metals to a composite surface with both metals and the underlying dielectric exposed. All factors that could damage the Cu surface must be controlled throughout the sequence (Liang, Martin, & Lee, 2001).

(c) 1.2.3 INTEGRATION AND FUTURE DIRECTION OF CMP

The interconnect metal of choice for at least a few more generations of advanced devices appears to be copper with continued tightening of process metrics such as dishing and erosion. According to the ITRS roadmap, maximum allowable Cu line thinning in an
array is already less than 15 nm and is projected to be only 6 nm by the 32 nm node (Brongersma, Beyer, & Maex, 2005). Achieving this target consistently in manufacturing will require slurries formulated to specific materials, pads with excellent surface texture control, and processes with razor-sharp endpoint and/or high selectivity to a stop layer. The dielectric film stack appears to be the next battleground for improving interconnects speed (Lotz, Matysek, & Schlaak, 2011). For most 65 nm process flows, cadmium oxide (CdO)-based materials are the dominant choice for low-k dielectrics. However, they are not porous and the effective k-value is > 2.5 in most cases. At the 45 nm node currently being developed, integration activities seem largely focused on extending the second-generation modified CDO films, preferably without introducing porosity if it can be avoided (Watanabe, Shibata, Idani, Nakamura, & Tamura, 2007). It remains to be seen how low the effective k-value can be pushed and what speeds can be achieved through this approach. As the industry moves forward into the 32 and 22 nm nodes, it is expected that devices will require ultralow-k (ULK) dielectric with k-value < 2.2 to achieve the desired performance targets (Schulze et al., 2004; F. Zhao, Economikos, Tseng, Kim, & Engbrecht, 2007). Issues of water absorption and chemical retention during CMP and post-CMP cleaning with porous ULK materials are driving most integration teams to include a capping or sealing layer. Unfortunately for CMP, all known ULK materials have a strong trend of lower mechanical strength with lower k-values, primarily due to required porosity (Schulze et al., 2004).

Typical mechanical failure modes include delamination, cracking, and inelastic deformation. As the industry transitions to these materials, the CMP process must
accommodate mechanical fragility of ULK by moving toward lower pressure and lower shear processes. Most copper and barrier polishing work for these applications is now focused at 2 psi and below, with some targets as low as 0.5 psi (X. Y. Liu et al., 2011; Sawyer, 2004). Semiconductor manufacturers are required to manage the economic aspects of their business in addition to technology. The goal of delivering products to their customers in spec, on time and at the lowest reasonable cost involves managing both production capacity and new product development.

Now that CMP is established as mainstream for advanced CMOS manufacturing, other technologies are attempting to leverage CMP to achieve the performance they need. These applications represent emerging growth areas and often hold significant planarization challenges of their own. Analog, mixed signal, and even power devices are now investigating advantages that can be realized in their unique process flows. Advanced packaging concepts and through silicon vias (TSVs) represent two more areas where planarization is key to successful technology deployment (Andry et al., 2008; Henry et al., 2008).

Even with the difficulties and uncertainties associated with some aspects of CMP, the planarization results are superior to any other process currently available. Nonplanarized surface topography is the result of the fabrication process that comes from the deposition of the film on a previously etched patterned surface. CMP achieves planarization of the nonplanarized surface. Loss of planarity arises during lithography. Several other factors, namely autofocus errors, residual lens aberrations, resist thickness...
variations, and water curvature associated with wafer perforations and with film stresses influence planarity. Only CMP is universally applicable to cause global planarization.

1.3 DEFECT DETECTION IN SUBMICRON ICs

Driving the challenges are semiconductor technologies that persist in following Moore’s law. Advent of new processing materials and new packaging styles, like flip-chip and chip-on-chip that sandwich internal circuit structures between the silicon substrate and the chip carries, only further complicate the matter (B. M. Rogers et al., 2009).

Key failure analysis (FA) will suffer in the face of these new developments, while others may become completely obsolete. The Sematech Product Analysis forum has identified three areas in need of immediate attention (McDavid, 1994; S. Smith, Tranfield, Bessant, Levy, & Lay, 2000):

- Developing physical logic-fault isolation techniques that can cope with dense flip-chip arts, subtle failure mechanisms, and gigahertz operating speeds.
- Developing software-based techniques of logic-fault isolation with the same abilities.
- Finding high-magnification, high-resolution methods for routine inspection to replace visible-light microscopy without sacrificing throughput.
Fault isolation has top priority. Physical fault isolation pinpoints failure locations on the basis of an IC’s emission of sensitivity to light, heat or electrons. But as the chip top, or front side, gets more crowded with metal lines and I/O, and the entire assembly is flipped over onto a substrate, internal circuits are cut off from front side methods. While procedures are emerging that exploit silicon’s relative transparency to infrared (IR) light, further development is critical especially for the measure of time-varying signals (Rajesh, C, Srivatsan, Harini, & Shanthi, 2008; Vallett & Soden, 1997).

Software based diagnostic tools take a completely different track. They compare the IC test data with logic simulation so as to narrow a potential fault list down to a few suspects. In order to optimize the power of software diagnostics for fault isolation, designers must consider the testability and diagnosability of their circuits. The advantage of some design-for-testability features (like adding special latches) must be balanced against their possible impact on chip area and performance. Further, current diagnostic techniques require design accommodations to ensure compatibility with nonstatic circuit designs like dynamic node, or precharge, logic, now seeing more use (Vinnakota, 1999). The reward is more-diagnosable designs that have a higher probability of first-silicon success and shorter debug time. A thorough analysis of the current state of the art software based diagnostic tools in use is discussed by Bertacco et al. (Constantinides, Austin, Mutlu, & Bertacco, 2007)

The third urgent need is for rapid, high-powered microscopy for routine inspection. While improved resolution and higher-magnification alternatives like electron
and scanning probe microscopy exist, they are slow and sense only near surface
topography (Nemanich et al., 1998; Weiss, Ogletree, Botkin, Salmeron, & Chemla, 1993;
Wu et al., 1998). Unless physical or software isolation methods are devised to localize
defects precisely (within a few micrometers), the time required for routine defect
inspection will soar dramatically. Further details on the current state of rapid high-
powered microscopy for defect detection are discussed in the next section.

A successful failure analysis involves a series of distinct activities that flow from
preparation to analysis and closure. The first step is understanding the failure conditions
and behavior. Errors in production testing can misidentify good ICs as failures. Initial
analysis procedures must ensure that suspect IC is still failing and that its behavior is
thoroughly understood. Historical information from similar failures, when available, can
provide clues.

The next step is duplicating the original failure behavior. More than one failure
mechanism may affect an IC, yet only one maybe responsible for the incorrect behavior.
Other mechanisms may have existed in the IC at the time the failure was observed or may
have been introduced afterward. Duplication, in the laboratory is essential so that the
proper electrical stimulus for various physical fault isolation techniques maybe applied.

Determining the root cause mechanism behind a failure is the most technically
involved, tedious and costly step of them all. It consists of a series of electrical and
physical measurements that will conclusively define an electrical fault or anomaly in
terms of the physical mechanism responsible. Fault isolation, determining where to look is key. Next comes deprocessing the IC films so as to reach the underlying layers for inspection or further electrical isolation. For more precision, internal microprobing (or other methods) further localizes and electrically characterizes a defect. Finally, physical inspection provides an image of the defect mechanism and the chemical and material properties that help identify its root cause.

Determining the root cause and documenting corrective action closes the case. The information obtained is used to make decisions and correct problems so as to improve design, fabrication, or test processes. IC companies must see to it that detailed information from the analysis is documented and communicated.

During the FA process, all applicable non-destructive FA techniques must be performed prior to the conduct of any destructive FA techniques. Table 1 shows the sample non-destructive and destructive techniques used in FA.

<table>
<thead>
<tr>
<th>Non-destructive Techniques</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Failure Verification</td>
<td>validation of reported failure</td>
</tr>
<tr>
<td>Optical Microscopy</td>
<td>external or internal visual inspection</td>
</tr>
<tr>
<td>X-ray Radiography</td>
<td>internal x-ray imaging</td>
</tr>
<tr>
<td>Curve Tracing</td>
<td>current-voltage characterization</td>
</tr>
<tr>
<td>Hermeticity Testing</td>
<td>check for hermetic sealing</td>
</tr>
<tr>
<td>SAM</td>
<td>detection of delaminations</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Destructive Techniques</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decapsulation</td>
<td>opening of the IC package</td>
</tr>
<tr>
<td>Sectioning</td>
<td>cross-sectioning of the sample</td>
</tr>
<tr>
<td>Hot Spot Detection</td>
<td>detection of heat-generating defects</td>
</tr>
<tr>
<td>LEM</td>
<td>detection of light-emitting defects</td>
</tr>
</tbody>
</table>
### Table 1.1: Sample destructive and non-destructive techniques to be used in failure analysis

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microprobing</td>
<td>Direct electrical analysis of the die circuit</td>
</tr>
<tr>
<td>SEM/TEM</td>
<td>High magnification real-time imaging</td>
</tr>
<tr>
<td>EDX/WDX</td>
<td>Elemental analysis</td>
</tr>
<tr>
<td>Focused Ion Beam</td>
<td>High resolution die sectioning/imaging</td>
</tr>
<tr>
<td>FTIR Spectroscopy</td>
<td>Chemical analysis</td>
</tr>
<tr>
<td>Auger Analysis</td>
<td>Surface analysis</td>
</tr>
<tr>
<td>SIMS</td>
<td>Compositional analysis</td>
</tr>
<tr>
<td>LIMS</td>
<td>Compositional analysis</td>
</tr>
<tr>
<td>ESCA or XPS</td>
<td>Surface analysis</td>
</tr>
<tr>
<td>AFM/STM</td>
<td>High-resolution probe imaging</td>
</tr>
<tr>
<td>EBIC</td>
<td>Induced current imaging of defects</td>
</tr>
<tr>
<td>OBIC</td>
<td>Induced current imaging of defects</td>
</tr>
<tr>
<td>Chromatography</td>
<td>Chemical analysis</td>
</tr>
<tr>
<td>RGA</td>
<td>Residual gas/moisture analysis</td>
</tr>
</tbody>
</table>

### 1.3.1 FAILURE ANALYSIS (FA): MICROSURGERY

This section provides additional details on the current state of imaging of IC’s for failure analysis. To perform the subsequent steps of microprobing and inspection, layers must be selectively removed, or deprocessed, either from the entire IC or from a small area over a circuit or structure of interest. A combination of wet chemical etching, reactive ion or dry etching, and mechanical polishing is used for removing an entire film. Focused ion beam (FIB) systems also serve routinely to remove and deposit materials in localized areas (Gerber & Dzimianski, 1973). Selectivity is critical to remove only the film of interest while also making sure not to remove the defect itself during the delayering process.

Inspection is accomplished using one or more forms of high-magnification microscopy to expand features and allow the defects and anomalies to be easily
visualized and identified. Optical microscopy and SEM are by far the two most utilized techniques (Lewis et al., 2000). Transmission electron microscopy (TEM) is a more sophisticated technique, which excels at high-resolution imaging of structures in cross section and characterization of material properties. SEM techniques such as scanning Kelvin microscopy, scanning capacitance microscopy, atomic force microscopy, and scanning-nearfield optical microscopy produce high-resolution physical and electrical images for inspection material analysis (Born & Wiesendanger, 1998; Gerber & Dzimianski, 1973; Lewis et al., 2000; Melitz, Shen, Kummel, & Lee, 2011).

Optical microscopy utilizing reflected light in the visible spectrum has proved capable of identifying many physical defects and was a mainstay in failure analysis (FA) for years. It also is able to image structures buried under transparent insulating layers such as silicon dioxide. But smaller features and defects have pushed the method to its resolution limit, around 0.2-0.3 µm as defined by the wavelength of the illumination source. Shorter-wavelength radiation, such as ultraviolet and X-ray, may improve resolution.

Confocal scanning optical microscopy (SOM) extends the technique somewhat through the use of a laser source and optics that pass only reflected, in-focus light. In this way focusing on only one vertical level in the IC at a time forms a sharp image with a narrow depth-of-field. The use of infrared lasers in the SOM permits observation through the back of silicon wafer or die, silicon being fairly transparent to IR. Images of an IC’s active regions can be obtained by using reflected IR microscopy with a resolution of 1.0 µm or so. This avoids problems due to power distribution planes and flip-chip
packaging; but interconnect levels are still buried and the spatial resolution is already insufficient for state-of-the-art technologies (Sanghera et al., 2008).

The SEM is an FA workhorse, providing magnification of up to 300,000 times. In a technology with 0.18 µm minimum features, for example the maximum tolerable defect size within the interconnection layers is about 0.06 µm, well below the limit of the optical microscope. Secondary electron imaging in a field-emission type SEM, the current state of the art, generates an image with a high, 2-5 nm spatial resolution and a large depth-of-field (Zontak & Cohen, 2009).

Scanning Probe Microscopy (SPM) looks like the most obvious solution for routine surface imaging with high magnification (Yu, 1996). A basic scanned-probe platform consists of an ultrasharp tip at the end of a flexible cantilever, an x-y positioning system, and an arrangement to monitor vertical (z-axis) displacement of the cantilever with the sample held stationary over the point of interest. The displacement is monitored and recorded to provide data used to construct an image. Variations of this imaging method include, scanning kelvin microscopy and scanning capacitance microscopy (Giannazzo, Raineri, Magna, Catania, & Sofia, 2005; S. E. Park, Nguyen, Kopanski, Suehle, & Vogel, 2006).

Numerous other modes have been reported including thermal, magnetic field, and high-speed voltage with 1-ps temporal resolution. Researchers at IBM Corp.'s Thomas J.
Watson Research Centre, N.Y., have demonstrated 1nm resolution using transmitted light through a thin sample (Wickramasinghe, 1990).

The migration of techniques from fairly quick low-magnification visible light microscopy to advanced methods capable of atomic-scale resolution creates a critical tradeoff for FA. High-magnification, high-resolution images take much longer to acquire because of tedious sample preparation, the need to de-layer and inspect levels serially, the need to scan surfaces slowly, and the need for data interpretation. While techniques like field-emission SEM, TEM, and SPM are highly capable, their routine use on isolated defective circuits and metal interconnect lines that may traverse hundreds of micrometers and numerous wiring levels will cause analysis cycle times to become prohibitively long.

Fault isolation is still key as previously mentioned. There is a desperate need for quicker methods that analyze surfaces in a short period of time and act as supplements to the more tedious methods by pointing out the areas of interest (defects) for further analysis using the regular methods. This is where the current research would come in handy. Determining the location of the defect is the most time consuming step. We address this issue by designing a novel and efficient method for the detection of surface topographical features using fluorescent nanoprobes. By tuning the size and chemical properties of these nanoprobes, the nanoprobes can elucidate the surface structure of large areas in a minimal amount of time. Once the site of defects is discovered advanced microscopy techniques can be used to determine the nature and cause of the defects.
1.4 INTERACTIONS OF NANOPARTICLES AND POLYMERS

In order to design an effective system, it is crucial to understand the nature of interactions between nanoparticles and polymer/Si substrates. This part of the chapter deals with these interactions.

The mixing of nanoparticles and polymers has been known for over a century. For example carbon black and zinc oxide has been used in automobile tires since 1837 (Goodyear, 1837). The first mass produced nanoparticles containing polymer composite was Bakelite, was introduced in the early 1900s (Baekeland, 1909). The most significant achievement, that accelerated the studies on interaction of nanoparticles and polymers, was the five-fold increase in the tensile strength and yield of nylon upon adding mica particles reported by engineers at Toyota (Y. Kojima et al., 1993).

Today, the advancement in research of nanoparticles reports a wide variety ranging from fullerenes, inorganic, dendrimers, carbon nanotubes, bionanoparticles etc. The precise shape and size of these particles, along with the development in the instruments that are used in the probing of these nanoparticles such as atomic force microscopes, electron microscopes, laser scanning microscopes etc., make it easier to study the interactions of nanoparticles and polymers (Balazs, Emrick, & Russell, 2006).

In order to develop polymer nanocomposites, the ability to control nanoparticle dispersion is very important. One of the methods employed to prevent aggregation is
adding layers of ligands on the surfaces of the nanoparticles. Ligands that are attached to the nanoparticles mediate the interactions between them and the polymers. Thus, in order to understand the interactions between polymers and nanoparticles it is essential to understand the surface modifications of the nanoparticles and then derive the correlation for the interactions between the two.

Studies on functionalized planar surfaces, including self-assembled monolayers (SAMs) (Bain & Whitesides, 1988) and polymer brushes (Husseman et al., 1999) on substrates ranging from gold to metal oxides led the evolution of surface chemistry in nanoparticle functionalization. Most conventional ligands lead to aggregation of the nanoparticles and hence replacement of these conventional ligands with those that interact favorably with the polymer host is the key in achieving uniform dispersions. Hence, versatile synthetic strategies to fine-tune the chemical nature of the ligands are needed. Some of the reported studies involving mild polymerization techniques, such as ring-opening metathesis polymerization and controlled free-radical polymerization, have proven very useful in grafting-from experiments, giving well-dispersed nanoparticles within a composite (Watson, Zhu, Nguyen, & Mirkin, 1999). In the case of low molecular weight polymer ligands or conditions where the nanoparticles are sensitive to the conditions of polymerization, the grafting-to approach has been applied (Korth et al., 2006). This has been effective for preparing polyethylene glycol-grafted (PEGylated) nanoparticles, which impart hydrophilicity and bio-compatibility to the nanoparticles (Hong, Emrick, & Rotello, 2004; X. Huang, El-Sayed, Qian, & El-Sayed, 2006)
To gain an insight into the fundamental factors that control particle dispersion, let us then consider the simplest filled polymer: nanoparticles in a single-component melt. The entropic interactions, though weaker than the dominant enthalpic interactions, play a significant role in dictating the structure (Hooper & Schweizer, 2006; Mackay et al., 2006). Computational studies on filled homopolymers near a surface containing a notch or a crack showed that the polymer melt induced an entropic depletion attraction between the particles and the surface drives a fraction of the nanoparticles into the defect filling it up. Gupta et al. showed experimental approach to nanoparticle migration. Multilayers comprised of PEGylated CdSe nanoparticles dispersed in poly (methyl methacrylate) (PMMA) in contact with a brittle silicon oxide layer were heated above the glass transition temperature of the composite induced cracking of the SiOx layer due to the difference in the coefficients of thermal expansion (Gupta, Zhang, Emrick, Balazs, & Russell, 2006). Nanoparticles that were comparable in size to the radius of gyration of the PMMA migrated into the cracks, as shown in the fluorescence optical micrograph in Figure 1.3.
Figure 1.3 Fluorescent image showing the quantum dots filling up of the cracks caused by the difference in the thermal annealing coefficient (S. Gupta et al., 2006)

This behavior however, was not observed in the case of smaller nanoparticles due to the substantial entropic penalty associated. These results suggest a route for designing self-healing systems.

Polystyrene (PS)–functionalized CdSe dispersed in PS matrix examined by Crosby and co-workers exhibited similar entropic interactions, in which nanoparticles were found to segregate to the tip of a crack (Fig. 1.4) and resulted in the modification of the crazing characteristics of the glassy polymer (J.-Y. Lee, Zhang, Emrick, & Crosby, 2006).
Figure 1.4 Transmission electron microscopy (TEM) image of 5-nm CdSe/ZnS nanoparticles with polystyrene (PS) ligands in polystyrene where a craze has been introduced to the film. A uniform dispersion of the nanoparticles is seen outside the crazed region. (J.Y.Le 2006)

Until now we have stressed on the importance of uniform dispersions of nanoparticles. This brings us to the question, if the aggregation phenomenon can be used to an advantage. A study reported used CdSe nanorods functionalized with alkane ligands in PS matrix. They observed that the system phase separates into domains of PS and nanorods due to the incompatibility of the polymer matrix and ligands. Upon the application of an electric field to the solution of nanorods mixed with PS, the nanorods aligned in the direction of the applied field and, as solvent evaporated, the PS and oriented nanorods phase separated. A close packing or “self-corralling” of the nanorods into a hexagonal array normal to the film surface is achieved by the minimization of the
interfacial energy between the domains (Ryan, Mastroianni, Stancil, Liu, & Alivisatos, 2006).

Figure 1.5 A TEM image of an ordered hexagonal array of 8-nm diameter CdSe nanorods (40nm in length) that resulted when a mixture with alkane ligands was mixed with PMMA in chloroform.

Nanoparticles assemblies were investigated in concert with surface patterning and interfacial interactions to create photovoltaic devices. The self-corralling was used to direct the lateral positioning of the ordered arrays of nanorods onto an underlying circuit (Ryan et al., 2006).

As previously mentioned one of the issues is a uniform dispersion even though they are chemically compatible. The polymers drive the aggregation within these systems
enhancing the volume that is accessible to the chains. These results can be the hypothesis for the conclusion that an entropically induced depletion attraction is caused by the polymers in the melt. Extensive studies have been done on the depletion attraction between colloids and confining surfaces in polymeric solutions or solvents. Series of studies relevant to our area of interest involved a solution containing a binary colloid mixture lying above a regular rough surface. The smaller particles drove the larger nanoparticles into depressions or wells in the rough surface. This was an interesting observation considering there have been polydispersity studies indicating small nanoparticles having a preference over larger nanoparticles when covering a surface (Zbigniew Adamczyk, Weronski, & Musial, 2001).

1.5 THIN FILMS ON PATTERNED SUBSTRATES

Understanding the stability on thin films on solid substrates is of significant importance to our research since it involves coating polymer thin films on scratched substrates for selectivity to the scratch. There has been significant interest in this area. The underlying mechanisms and forces involved are some of the aspects we will cover. All real surfaces exhibit two heterogeneities: chemical and physical (characterized by the roughness). Some of the recent studies have focused specifically on their wetting behaviors where the surfaces are characterized by regular corrugation of a defined structure and/or a well defined lateral variation of surface energy (Robbins & Andelman, 1991). Along with throwing light onto the wetting behavior they also can be used to create liquid microstructures. Furthermore, changing the degree of polymerization, without significantly influencing the surface and interfacial energies involved, can easily
control both the viscosity and the molecular size.

Preparation of patterned substrates has been achieved through various routes and has been widely researched and reported (X.-mei Zhao, Xia, & Whitesides, 1997). Lithography has been the choice for producing micron and sub-micron size patterns. Lateral dimensions of the patterned area decreases with pattern size with this technique. Self-assembly processes have also been used to create patterns over nanoscopic characteristic length scales. Mayes et al. produced saw-tooth like surface morphologies using mis-oriented silicon single crystals (Fasolka, Harris, & Mayes, 1997). Rusell et al. created regular chemical heterogeneous surfaces using glancing angle metal evaporation on silicon surfaces (Rockford, Liu, Mansky, & Russell, 1999).

Krausch et al. have considered the stabilities of thin polystyrene (PS) films on silicon substrates with a saw tooth or corrugated structure (Rehse et al., 2001). These substrates were prepared by ultrahigh vacuum annealing of suitably miscut silicon single crystals. Nanoscopic corrugations of well-defined mean spacing are developed over macroscopic distances due to a surface faceting transition. A thin polymer film of average thickness \( t_{av} \) was spin cast onto these substrates from a solution of toluene and the authors observed that the film surface follows the corrugations. The surface tension is known to minimize the curvature in the film and hence the rounded edges, and the thickness varies laterally (i.e., thicker in the troughs and thinner on the peaks)
One can be free to assume that the free energy of polymer thin films on heterogeneous substrates will exhibit lateral variations. To really understand the role of chain confirmation and confinement in thin films, one needs to analyze if the chains retain a statistical random walk distribution or not near a hard boundary. Silberg et al., argued that the chain confirmations remain Gaussian near the surface under the assumption that the wall reflects the part of the chain that statistically cross a hard wall (Silberberg, 1982). This would suggest that the chains retain their statistical distribution, which would imply the lack of a driving force for instability and dewetting in thin films. Other studies have demonstrated that chain ends induce a long-range repulsion from walls acting over a distance of $R_g$, leading to a small driving for dewetting (Semenov, 1996). N. Rehse et al. proposed that in the case of confined films, chains try to move into the thicker regions in order to reduce the distortions induced by surfaces hence triggering dewetting. In the case of thicker films, the increasing number of chains makes it difficult to be distorted by the boundary surfaces (Rehse et al., 2001).

Since the total free energy of the system does not change by an exchange of the undistorted chains between regions of different film thicknesses, films thicker than some critical are expected to remain stable against dewetting. This critical thickness should have a length scale of order $R_g$. Simulations on the shape of polymer chains in a melt supported this theory. According to the authors, the chain ends are not located next to each other, and so the polymer chain is actually longer on an axis connecting the chain ends leading to a cigar formation of the polymer chain. The change in the polymer size perpendicular to the line joining the chain ends is reported to have very little change.
Based on this the authors concluded that the polymers close to the hard walls will align themselves such that their long axis is parallel to the wall to avoid confinement. This however when applied to thin films would not work accurately as there will be distortions in the chain confirmation for very thin films and dewetting would occur. We will not discuss the subject further but Pakula et al., have extensively studied the subject and can used as reference (Pakula, 1991).

1.6 NANOPARTICLE DISPERSION

Spherical colloids have been the dominant subject of research for many decades due to their ease of production as monodispersed samples (E Matijevic, 1994). Driven by the minimization of interfacial energy, a sphere represents the simplest form that colloidal particles easily adopt during the nucleation or growth process. A wide variety of chemical methods have now been developed to generate spherical colloids from a range of different materials such as organic polymers and inorganic compounds (Fink, Stober, & Bohn, 1968). It has also been possible to achieve a precise control over the properties of spherical colloids by changing their intrinsic parameters such as the diameter, chemical composition, bulk substructure, crystallinity (polycrystalline versus amorphous), and surface functional group (thus the surface charge density and interfacial free energy) (Egon Matijevic, 1981). It is evident that the adsorption of nanoparticles on the surface of a polymer is the first step towards a “two-dimensional” nanocomposite. But for the design of these systems knowledge of the kinetics and mechanism of adsorption is essential. Numerous theoretical and experimental works have been published that are specifically devoted to the knowledge of the kinetics and mechanisms
of nanoparticle dispersion. A comprehensive review containing a very thorough analysis on the kinetics of adsorption of micrometer and submicrometer colloidal particles from both the quiescent and moving dispersion medium on surface with various geometries of nanoparticles like planar, cylindrical and spherical etc. has been done by Adamczyk et al., (Z Adamczyk, Siwek, Zembala, & Weronski, 1992). The authors contributed mostly to the understanding of the model of random sequential adsorption as well as to the kinetics of the process.

The experimental data on the kinetics of adsorption is ambiguous for the various natures of nanoparticles that have been studied. Adsorption of gold nanoparticles on polymer surfaces has been systematically studied. Shull et al. have reported the equivalent change in the thickness of the gold nanoparticles layer on the surface of polyvinlypyridiene films with respect to time (Shull & Kellock, 1995). The results were in coherence with the model of irreversible diffusion limited adsorption. Similar results were obtained on surfaces functionalized with poly (allylamine) hydrochloride. Effects of polydispersity have been studied by Hanarp et. al., where the smaller nanoparticles are shown to adsorb preferentially over larger nanoparticles (Hanarp, Sutherland, Gold, & Kasemo, 2003). The power law that describes the kinetics of adsorption of larger particles on a surface already occupied by smaller particles is:

$$\theta^\infty - \theta \sim \tau^{-1/2}$$

(where $\theta^\infty = 0.547$ is the maximal cover- age of the surface at infinite time of adsorption (Z. Adamczyk, 1992).
Dokou et al., have accounted for effects of gravity on the kinetics of adsorption of nanoparticles (Dokou, Barteau, Wagner, & Lenhoff, 2001). Atomic force microscopy was used to compare the amount of particles adsorbed on 1 sq. micron surfaces arranged horizontally and vertically, thus obtaining notably different values for various particles and sizes (polystyrene latex, silica, gold). In another study showing the effect of gravity was shown on the adsorption of lipid vesicles on gold surfaces (Hanarp et al., 2003). The gold surfaces, hydrophilic and hydrophobized with monolayers of alkanethiols demonstrated step-wise change in the adsorbed mass during the first several minutes of contact between the colloidal solution and the quartz crystal resonator. Sastry et al. reported a series of works studying the adsorption of Au, Ag, and CdSe nanoparticles from hydrosols of various concentrations at various pH values on thin films of octadecylamine and self assembled monolayers of thiols with the NH2 end groups (Gole, Sainkar, & Sastry, 2000; Sastry, Mayya, & Bandyopadhyay, 1997; Sastry, Patil, & Sainkar, 1998). The experimental kinetic curves had two distinct parts: a linear increase in the mass of adsorbed particles with respect to time, and a plateau indicative of no changes in mass.

Research suggests various factors affect the adsorption of nanoparticles: size and polydispersity, coverage of the layer, pH of the colloidal solution and the nature of interactions with the surface.
1.7 SELF ASSEMBLY OF NANOPARTICLES ON SURFACES

In order to understand the adsorption of nanoparticles on the substrates for our research, an in depth understanding of the forces driving self-assembly is critical. This has in fact been the focus of study for the last two decades by Adamczyk et al., (Adamczyk et al., 1992). The various forces that are involved in the formation of particle layers on surfaces are,

a) capillary forces that arise pulling particles together when the solvent layer thickness becomes smaller than the particle diameter;

b) electrostatic interactions resulting in the repulsion between like charged particles and their attraction to oppositely charged surfaces;

c) van der Waals forces that occur at very low distances and play a prominent role in the formation and stabilization of particle aggregates and 2D crystals. A description of these forces is shown in Figure 1.6 (Burkhardt, Fuchsberger, Nisch, & Stelzle, 2010).

A consequence of charged surfaces of both the particles and the substrates is long-range electrostatic repulsion. It results in the repulsion of like charged particles and the attraction of particles to a surface bearing charge density with the opposite sign. The critical parameters for controlling strength and range of electrostatic interaction are the charge density of both the particles and substrate as well as the ionic strength of the buffer solution in which the particles are immersed. Both are reduced in the presence of mobile ions in the buffer solution. For example polystyrene particles exhibit negative surface charge due to the presence of sulfonate groups stemming from polymer synthesis. Semmler et al. (Semmler, Mann, & Ric, 1998) and Hanarp et al. (Hanarp et al., 2003)
demonstrated the control of particle coverage by variation of the salt concentration. In effect, repulsion of like charged particles is reduced or completely suppressed

![Diagram showing forces involved in formation of particle layers](image)

Figure 1.6 Forces involved in the formation of particle layers on surfaces a) capillary, b) electrostatic interactions, c) van der Waals forces

by the addition of mobile ions. Though the kinetics of adsorption is dependent on the particle concentration, the final surface coverage obtained upon saturation is observed to be a function of only the ionic strength.

If the interparticle distance falls below a critical limit then the van der Waals interactions come into play. The particles tend to attract each other and tend to form agglomerates and the interparticle distance is dictated by the particle size itself. These mechanisms have been studied extensively in colloidal physics and have been used for devising stable colloid formulations (Hiemenz & Rajagopalan, 1997).

The influence of surface charge of the substrate on the particle assembly has also been investigated. Serizawa et al. investigated the kinetics and coverage obtained upon the adsorption of polystyrene particles on substrates coated with ultra thin polymer layers
(Serizawa, Kamimura, & Akashi, 2000; Serizawa, Takeshita, & Akashi, 1998). Surface charge density was modulated by variation of ionic strength of the buffer used during the deposition of polyelectrolyte multilayers. Interestingly, the adsorption of polyelectrolyte multilayers that have been prepared using higher salt concentration in the buffer proceeded faster and resulted in higher coverage and as expected, no particle adsorption was observed on surfaces bearing like signed charge as the particles. The surface charge can also be modulated by variation of pH if an appropriate substrate material is used. An example with sapphire substrates was shown by Antelmi et al. and with mica substrates by Semmler et al (Antelmi & Spalla, 1999; Hanarp et al., 2003; Semmler et al., 1998; Serizawa et al., 2000, 1998). At the point of zero surface charge density (PZC) no particle adsorption was observed.

Capillary forces are a result of the surface tension between the solvent and the particle material. After application of a droplet of a particle suspension onto a substrate, during the controlled withdrawal from a suspension, during spin coating or after adsorption of particles to a substrate in a particle suspension, during spin coating or after adsorption of particles to a substrate in a particle suspension, the evaporation of the solvent plays a critical role with respect to the structure of the particle layer (Antelmi & Spalla, 1999; Hanarp et al., 2003; Semmler et al., 1998; Serizawa et al., 2000, 1998). As the thickness of the solvent layer becomes comparable to the particle diameter, attractive forces arise pulling particles together to form 2D crystals. Depending on the application this has been pursued as an advantage and a disadvantage. For example densely packed
crystals have been employed as masks during metallization process leading to regular arrangement of separated metal particles.

1.8 NANOPARTICLES AND DEFECTS

With respect to defects, nanoparticles until today have been mostly used in the design and development of self-healing materials. The basic technique, which has commonly been applied, involves design of materials with auto-assembly properties.

Tsukruk and coworkers prepared nanocomposite membranes obtained by spin-assisted layer-by-layer assembly of polymeric monolayers with a metal nanoparticle intralayer. The thickness was 35-55 nm. The gold nanoparticle layer contains 13 nm gold nanoparticles. These were sandwiched between alternating layers of polyelectrolytes. Upon plastic deformation, the membranes exhibited a complete and autonomous recovery of the properties in hours (C. Jiang, Markutsya, & Tsukruk, 2004).

Computer simulations have helped in designing nanostructures with self-healing properties. These have helped to formulate better particles while eliminating unsuccessful ideas that would struggle when translated to real applications. Janus nanoparticles composed of hydrophilic and hydrophobic portions are a good example. Researchers have studied their self-healing properties when embedded in a lipid bilayer membrane. The results indicated that, during an external compressive stress on the membrane surface in an aqueous environment, Janus nanoparticles can self assemble on the edge of a pore,
with hydrophilic ends facing the inner of the pore. This assembly did not effect on the integrity of the membrane (Alexeev, Uspal, & Balazs, 2008).

Nanoparticles are currently being used as mobile carriers, with healing functionalities in solid and liquid environments. This is based on the exploitation of intermolecular interactions and maximization of entropy changes. Balazs et al. first simulated and later experimentally demonstrated the migration of nanoparticles embedded in a polymer matrix to the damaged area where a fracture has occurred (K. A. Smith, Tyagi, & Balazs, 2005). The driving force is the gain in conformational entropy of polymer chains by the expulsion of particles. The particle size and surface functionalization are the important parameters. Small particles compared to the relatively larger particles would not do the same thing. An example of this was discussed in section 1.4 where CdSe/ZnS particles coated with PEO percolated to the crack in the Silicon layer caused due to the difference in coefficient of thermal expansion as shown in Fig. 1.3.

The effectiveness of various approaches has not been completely demonstrated for self-healing. They could however be used in multiscale repairing for recovery of functional properties like electrical conductivity or mechanical performance. We can conclude that auto-assembly is a simple mechanism that operates at different length scales. At the macroscale, examples of hourglass shaped polyurethane beads patterned with copper patches, or electromechanical systems have shown self-healing properties.
The numerous examples and studies reported in this section are clear indications that nanoparticles and defects are closely associated. Most applications of nanoparticles with respect to defects have been towards self-assembly and healing, while applications towards the detection of defects have been limited.
In this section the materials used in the analysis will be discussed. A brief introduction to methods of analysis will also be included.

2.1 MATERIALS

2.1.1 POLYSTYRENE

Homopolymer Polystyrene of 192,000 Da molecular weight (Mn) and 350,000 Da (Mn) obtained from Sigma Aldrich are used for the study without further purification. The polydispersity of the polymers was reported to be 1.2 and 1.18, respectively by Sigma Aldrich.

2.1.2 PMMA

Polymethylmethacrylate was obtained from Sigma Aldrich and used as received. Gel permeation chromatography was used to obtain the number average molecular weight of 150,000 Da and the polydispersity of 1.1 as reported by Sigma Aldrich.
2.1.3 TOULENE

ACS grade Toluene of 99.5% purity was obtained from Sigma Aldrich and used as received.

2.1.4 QUANTUM DOTS (QDs)

The quantum dots were obtained from Dr. Matthew L. Becker’s research laboratory at the University of Akron. The preparation of these quantum dots is discussed in the paper by Becker et al. (Alexeev et al., 2008). The absorbance and luminescence spectra of the quantum dots synthesis by the method described is shown in the Figure 2.1. The quantum dots were dispersed in deionized water and were negatively charged as reported in literature. The average size of the quantum dots was 4nm with spectral absorbance at 470 nm and emission at 560 nm. The fluorescence yield (Φf) based on these values was calculated to be 0.84.
2.1.5 POLYSTYRENE NANOSPHERES

The polystyrene nanospheres (PS-NP) were obtained from Corpuscular Inc. (Coldspring, NY). Plain fluorescent nanospheres were used as received for this study. The polystyrene nanoparticles have an inherent negative charge due to the presence of sulfonate groups stemming from polymer synthesis. The zeta potentials ($\zeta$), as reported by Corpuscular Inc., of the 40nm particles was $-42.7\pm6.4$ mV and that of the 200nm particles was $-27.8\pm2.2$ mV indicating an anionically charged surface. A 2 ml solution of 1% concentration cost 190$. 

![Absorbance and Luminescence Spectra](image)

Figure 2.1: Absorbance (dotted) and luminescence spectra of CdSe/ZnS nanoparticles in PBS buffer. Numbers indicate the emission maximum of each sample. Dashed black lines represent fluorescence spectra after 120 days of storage in PBS under ambient temperature and atmospheric conditions. (M. D. Roy, Herzing, Lacerda, & Becker, 2008)
2.1.6 SILICON WAFERS

Silicon (100) wafers were purchased from Silicon Quest Int’l. (San Jose, CA). The silicon wafers have hydroxyl functionality at the surface as shown in (M. D. Roy et al., 2008). The silicon wafers were cut into 2cm*2cm sizes. They were cleaved along the 100 plane resulting of breakage in straight lines. They were subsequently cleaned using ozone. Cleaning the Si wafers with ozone enhances OH density and burns away organic contaminants.

![Figure 2.2: Depiction of the silicon wafer](image)

2.1.7 PATTERNED SILICON WAFERS

The patterned silicon wafers were obtained from Dr. Ho-Cheol Kim, IBM Research Division at the Almaden Research Centre, CA. These wafers had patterns of varying design, with varying depths and widths. These substrates were extensively used for analysis. Further analysis and images are added in chapter 3 during the discussion of detection of defects on patterned substrates.

2.1.8 CU DEPOSITED SILICON WAFERS

Large 8 inch diameter Chemical Vapor Deposited Cu on Si substrates were obtained from Dr. Ronald Jones in the Polymers Division at NIST and used as received.
by cleaving smaller pieces. The deposited layer was 10 micron thick as analyzed by AFM scratch test.

2.2 EXPERIMENTAL PROCEDURE

2.2.1 CLEANING OF SILICON WAFERS

The silicon wafers were cleaned by sonicking in toluene, methanol, and deionized water to remove any dust particles as well as organic contaminants. The wafers were stored in the final solution of deionized water. Dried with Kim wipes they were finally purged in a jet of nitrogen gas. At this point, they were immediately used in the experiments.

2.2.2 PREPARATION OF PS AND PMMA SOLUTIONS

PS and PMMA solutions were prepared by mixing the respective polymers in toluene in a Teflon capped glass vial. Teflon caps were used in order to prevent the toluene from reacting with the otherwise plastic caps thus contaminating the solution. The solutions were mixed for 4 h in case of PS, and overnight to prepare fully dissolve PMMA solutions. The solutions were then filtered with 0.45 \( \mu \)m PTFE filter and left over night to equilibrate.

2.2.3 SCRATCHING THE SILICON WAFERS

Silicon wafers were scratched in order to create artificial defects on them. This was done using an ordinary glass scribe with the sleight of the hand while trying to
maintain uniform pressure during the process. One large sample then was chipped into multiple pieces and used for analysis. We do realize that is not the most accurate way for replicating scratches but we justify our approach with the fact, that no scratch on any two substrates is ever the same. The wafers were then cleaned using the above-mentioned procedure.

2.2.4 SPIN COATING SOLUTIONS

Cleaned wafers were coated in a Laurell WS-400-6NPP-LITE environmental controlled spin coater. Various volumes of the solution, polymer concentrations, and spinning speeds were used to attain polymer films of different thicknesses.

2.2.5 SCRATCHING COATED FILMS

In the experiments where thin polymer coated silicon wafers were scratched to create defects in the films, a Swann Morton cygnetic 10 blade of 300 \(\mu\)m width was used to induce the scratches. The blade was dropped perpendicular onto the film surface and pressure applied and removed. This procedure on analysis proved to be giving us uniform defects and was used for the step heights experiments, which shall be described later in the chapter while discussing results.

2.2.6 EXPOSING SUBSTRATES TO NANOPARTICLES

The coated substrates were then exposed to the nanoparticle solution by two different methods. The first method involved a time-based approach where the samples
(coated silicon wafers) were flooded by the mixture of the 1% nanoparticle solution (the nanoparticles were dispersed deionized water) and deionized water in equal ratios. This approach helped us in doing a time-based study on the adsorption. 5, 10, 30, 60 and 90 minutes were the various times of adsorption used in the analysis. The second method involved dipping the samples vertically into the nanoparticle solution and removing it instantaneously and rinsing them in a vial of deionized water by dipping it vertically and pulling it out in a single motion. Fresh water vial was used every single time. A depiction of the method is shown in Figure 2.3.

![Figure 2.3 Scratched substrate exposed to nanoparticles by drop casting. The red portion is the nanoparticle solution. Not to scale](image)

2.3 MEASUREMENT INSTRUMENTS FOR ANALYSIS

Atomic force microscopy (AFM) was performed using a Dimension V AFM (VEECO Instruments) at room temperature in air and the AFM images were obtained in tapping mode. Commercially available etched Si cantilever with a spring constant of ~42 N/m and resonant frequency of ~330 kHz were used. NanoScope 7.30 software was used for data recording and surface roughness estimation. Optical images were taken with an Olympus microscope equipped with bright field and fluorescence light.
CHAPTER III

RESULTS AND DISCUSSION

In this chapter we aim to model and detect defects using fluorescent nanoparticles. We study by artificially creating defects using a glass scribe on Si and Cu substrates, which were chosen as the substrate in order to replicate integrated circuits. Polymer thin films were spin coated on these substrates for practical relevance to defects in polymer film coated substrates, as well as from finely tuning and enhancing the detectability of defects by nanoparticles.

3.1 SCRatched SUBSTRATES

This section of the results deals with the silicon substrates that are scratched using a glass scribe to replicate a random type of defect that can occur in CMP. This is the most common problem in the semiconductor industry. The goal of this analysis is to design a system, where the nanoparticles are driven to the specific defects (artificially created) on the substrate and elucidate them under a fluorescence microscope.
We initially started this study with quantum dots (QD) as these are relatively small in diameter 4-10 nm, and have inherent fluorescence due to the quantum confinement effect. We did a time-based study on the adsorption of quantum dots on plain silicon wafers that have scratches. From Figure 3.2, we can conclude that 4 nm quantum dots adhere randomly on the substrate. This adsorption negates the idea behind the study. The goal of the study was to design a imaging method for failure analysis where in the nanoparticles are driven to the sites of defects only. As the time allowed for adsorption increased, the fluorescence intensity also increased.

Figure 3.2: Adsorption of Quantum Dots on plain Si wafers that were scratched a) 5 mins, b) 15 mins, c) 30 mins
Since the goal was to use fluorescence microscopy as an alternative to the traditional methods of analysis, we looked for alternative particles that were fluorescence responsive and cost effective at the same time. Plain fluorescent PS nanospheres (PS-NP) were ideal candidates for this purpose. The particles were negatively charged similar to the quantum dots. The charge prevents agglomeration of the particles due to repulsions. As discussed in the introduction, the surfaces have zero charge density, which prevents the adsorption of particles due to surface charges. Their similar fluorescence characteristics allowed us to proceed with the analysis with small changes in the procedure. Even though the cost of 2 ml of 40 nm 1% PS-NP solution is relatively high (190 $), it was estimated that in comparison to the cost and time involved in running SEM it would still be cost effective. 2 ml solution can cover an area of around 6400 sq. inches or four 15” wafers.

At first, the scratches on the substrate were exposed to the PS-NP particles in similar manner as in case of QD. Again, we observed that the particles adhere everywhere (fluorescent region) on the substrate as seen in Figure 3.3 without specific selectivity to the scratch. The dark regions indicate the silicon oxide layer. The PS-NP particles, as discussed in the materials section, were copolymerized PS and fluorescence. This led us to believe that there is a presence of –OH groups on the substrate, which resulted in attractive interactions between the nanoparticles and formation of hydrogen bonds. We see the hydrogen bonds as the root cause for the particles adsorbing on the –OH rich surface of the substrate.
In order to eliminate the specific –OH interactions, a polymer layer was introduced to coat the substrates. In a paper by Miriam Rafailovich et al. (Rafailovich et al., 1996), the authors studied the dampening on Fourier components of patterned substrates that define the sharpness of the pattern by coating conformal polymer films of different thicknesses. PS with two molecular weights was used low molecular weight (>300 KDa) and high molecular weight (>1000 KDa) to study the effect of the polymer films. They observed that the lower molecular weight films behaved as frozen liquids, while in the case of higher molecular weight polymer films viscoelastic forces...
dominated. They showed that even a thin film of 680 Å thickness formed a non-uniform coating on a 130 Å grating. We gain better understand of the mechanism of thin polymer films formation on rough substrates by analysis of their results. Essentially they showed that sharper features are smoothed out in very thin films and as the overlayer polymer films get thicker, the longer wavelength features are progressively damped (smoothed) out. This provides us with a strategy to study the film thickness effects of polymer films on defect-coated surfaces to control detectivity levels.

Figure 3.4: Dampening of Fourier components on a patterned substrate. Rafailovich et al.

Thus, even though at first we expected that thick polymer layer would cover up the defects, we then realized that by maintain the film’s thickness to a minimum, we should
be able to obtain a uniform (conformal) polymer layer that would sustain the surface
defect features over wide range of wavelengths and amplitudes.

We studied the effect of various thicknesses of the film in order to ascertain the
best possible thickness. The variations in the spin speeds and concentration resulted in
the varying thickness of the film. Table 3.1 summarizes the various thicknesses obtained
from used parameters sets.

<table>
<thead>
<tr>
<th>Concentration/Spin Speed</th>
<th>2500rpm</th>
<th>5000rpm</th>
<th>8000rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1%</td>
<td>18nm</td>
<td>14nm</td>
<td>8nm</td>
</tr>
<tr>
<td>1%</td>
<td>57nm</td>
<td>45nm</td>
<td>35nm</td>
</tr>
<tr>
<td>2%</td>
<td>110nm</td>
<td>90nm</td>
<td>70nm</td>
</tr>
<tr>
<td>3%</td>
<td>175nm</td>
<td>150nm</td>
<td>125nm</td>
</tr>
<tr>
<td>4%</td>
<td>250nm</td>
<td>220nm</td>
<td>200nm</td>
</tr>
<tr>
<td>5%</td>
<td>370nm</td>
<td>320nm</td>
<td>270nm</td>
</tr>
</tbody>
</table>

Table 3.1: Variations of spin speed and thicknesses resulting in variations in thickness of
the PS layer.

From AFM analysis the average depth of the scratch was found to be in the range
between 350 nm – 700 nm. The AFM image of a scratch is shown in (Rafailovich et al.,
1996). The roughness ($R_q$) was averaged to 120 nm.
Figure 3.5: AFM height image of an artificially created scratch.

The coated substrates were then exposed to the nanoparticles by the procedures described in section 2.2.6.

3.1.1 FILMS PREPARED FROM 1 wt.% SOLUTION OF PS

We started the process of coating the scratched substrate with thin films prepared from 1 wt.% PS solution in toluene. By varying the spin speeds, the thickness of the films was being changed and the thinnest films were chosen for the further use in our study. Here, the films thicknesses between 8 nm and 18 nm were used. One of the most important observations was a presence of irregularities in the films not only around the scratches, but also in many other random locations on the surface. We think that the
presence of these irregularities around the scratches meant that the polymer layer did not uniformly cover the scratches. On the other hand, the roughness of the scratch, as previously discussed, is the negating factor, since we don’t have a good control over its depth and size.

Exposure time optimization

The scratched silicon wafer coated from 1% PS at 3000 rpm resulted in film of average 60 nm thickness. Substrates prepared in that way, were exposed to 1% PS-PN aqueous solution at varying exposure times. Used time periods were: 5 min, 10 min, 30 min, 1 h, and 3 h.

5 min exposure time

Images using fluorescent microscopy were taken to visualize the PS-NPs absorption.

Figure 3.6: Scratched substrate with 1% film-57nm. 5 min exposure time; before sonication (a), after 10 min sonication (b). The scale bar is 100 microns.
10 min exposure time

Figure 3.7: Scratched substrate with 1% film, 45 nm. 10 min exposure

1hr exposure time

Figure 3.8: Scratched substrate with 1% film, 45 nm. 1hr exposure: before sonication (a), after 10 min sonication (b)
3hr exposure time

Figure 3.9: Scratched substrate with 1% film, 57nm. 3hr exposure

The time exposure experiments were carried out to evaluate the most efficient time for the highest PS-NP absorption. Even though we were unable to quantitatively estimate the amount of PS-NP aborted on the surface, we could visually evaluate that the fluorescence intensity increases with increasing time, as expected. At the same time, it is observed that very short exposure time, 10 minutes, was sufficient to effectively outline the defects.
3.1.2 FILMS PREPARED FROM 2 wt.% SOLUTION OF PS

In this section we will discuss the results obtained using 2% PS solution. The spin coated film’s thickness varied between 35 – 57 nm. The fluorescence images of the surface showed no significant difference before and after sonication as shown in Figure 3.10. It also needs to be pointed out, that it was extremely difficult to obtain images of the exact area before and after sonication. On the few occasions, that it was possible, see Figure 3.8, the images looked almost identical and thus we concluded that sonication does not influence the adsorption of the PS-NP.

5min exposure time

a) 

b)

Figure 3.10: Scratched substrate with 2% film, 105nm. 5min exposure: before sonication (a), after 10 min sonication (b).
10min exposure time

Figure 3.11: Scratched substrate with 2% film, 110nm. 10min exposure, an arrow points at random PS-NP adsorption.

One must note that there is inherent fluorescence in the background. This is attributed to the organic layer (polystyrene).

30min exposure time

Figure 3.12: Scratched substrate with 2% film, 110 nm. 30 min exposure to nanoparticles
1hr exposure time

Figure 3.13: Scratched substrate with 2% film, 110 nm. 1hr exposure to nanoparticles

From fluorescence analysis, (Figure 3.9- Figure 3.13) of the 1% and the 2 % polystyrene coated films we can clearly see that the nanoparticles do not adhere to the coated substrate very well and the created defects are not clearly visualized. This can be attributed to the fact that the films are very thin when compared to the depth of the scratch and do not cover the scratch uniformly. The roughness of the scratch plays a vital role in this phenomenon. Since the scratch has a roughness on the order of 50 nm and the films’ thickness does not exceed 70 nm the films cannot fully cover the undulations of the surface. The films break down and form nonuniform films on the scratch, which limits PS-NP adsorption. Most of the images from the 1% and 2% film thickness show patchy adsorption of the particles on random areas of the substrates, for example in Figure 3.11 an arrow point to one of these agglomerations. This is explained in section 3.2.
3.1.3 FILMS PREPARED FROM 3 wt.% SOLUTION OF PS

In the current section the images correspond to film thicknesses ranging from 125 nm to 175 nm. This range is one of the most promising ranges for detection of the created defects. We can see clearly that even after a very short exposure to the PS-NP solution, Figure 3.14, the fluorescence outlines mainly the created scratch.

5mins exposure

Figure 3.14: Scratched substrate with 3% film, 175nm. 5min exposure
10mins exposure time

Figure 3.15: Scratched substrate with 3% film, 150nm. 10min exposure

1hr exposure time

Figure 3.16: Scratched substrate with 3% film, 150nm. 1hr exposure
From the images in Figure 3.14- Figure 3.17, it is evident that the scratches in the films are very clearly elucidated. The images are similar before and after sonication and hence have not been added for all the times of study. Clearly the scratches show detectivity and upon sonication. The nanoparticles adhere to the area where there is an enhanced contact and in this case, the V shaped grooves resulting from coating of the scratches with a polymer thin film provide the enhanced contact.
3.1.4 FILMS PREPARED FROM 4 wt.% SOLUTION OF PS

In the current section the thickness of the polymer films ranges from 200 nm to 260 nm. As in the case of the films prepared from 3% PS solution, this range of thicknesses allowed for highlighting of the scratches that we created artificially on the substrate.

5min exposure time

Figure 3.18: Scratched substrate with 4% film, 250nm. 5min exposure

Based on the images in Figure 3.19, an observation is made that the fluorescence intensity slowly starts to decrease as the film thickness approaches 250 nm. As it was also observed with very thin films, the thickness of the film covering the scratch has a very strong influence on PS-NP absorption. We will address this trend in the following section.
10min exposure time

Figure 3.19: Scratched substrate with 4% film, 250nm. 10min exposure

1hr exposure time

Figure 3.20: Scratched substrate with 4% film, 210nm. 1hr exposure

3.1.5 FILMS PREPARED FROM 5 wt.% SOLUTION OF PS

In this section we consider polymer film thicknesses ranging from 270 nm to 370 nm. These images are in a stark contrast to the images obtained from the 3% and 4% films. This can be attributed to the fact that films were thick enough to cover the scratch.
completely. We have confirmed this by scanning the coated scratch area with AFM imaging as shown in Figure 3.27. At these thicknesses, the PS films are no longer able to outline the scratch but slowly with increasing thickness the polymer covers the defect completely. The amplitude dependency on conformality of polymer thin films is discussed in the paper by Miriam Rafailovich and has been discussed previously.

5min exposure time

Figure 3.21: Scratched substrate with 5% film 270nm. 5min exposure
10min exposure time

Figure 3.22: Scratched substrate with 5% film, 300nm. 10min exposure

30min exposure time

Figure 3.23: Scratched substrate with 5% film, 270nm. 30min exposure
1hr exposure time

Figure 3.24: Scratched substrate with 5% film, 350nm. 1hr exposure

3hr exposure time

Figure 3.15: Scratched substrate with 5% film, 320nm. 3hr exposure
Figure 3.26: Scratched substrate with 5% film, 320nm. 3hr exposure and sonicated in distilled water as described in chapter 2.

From the set of data in Figure 3.21- Figure 3.26 we observe that the scratches are not highlighted with PS-NP, which is due to PS coating filling up the defects. On the other hand, we see a number of random defects that strongly attract PS-NP, Figure 3.23.

Figure 3.27: AFM height image of 5%, 300nm PS film on a scratch of $R_q = 130$nm
3.2 COATED AND SCRATCHED

During the set of experiments described in section 3.1, we observed that the nanoparticles adhered to random areas of the substrate, outside of the created scratch defects. Upon further investigation we also determined that in these areas the thin film showed significant surface irregularities. The nanoparticles were attracted to these surface features. We think that these unplanned irregularities are caused by one of the following sources:

(1) Defects of silicon wafers,
(2) Sedimentation of dust particles, or
(3) Solvent evaporation during spin coating.

Since we do not can control appearance of the unplanned irregularities, we decided to create defects within a polymer film that would simulate an irregularity. To illustrate this idea, we coated an unscratched bare wafer substrate with PS thin films and then randomly created a scratch on the film surface. Next, we exposed these substrates to the PS nanospheres solution. Dipping the sample and immediately removing the substrate from the solution did the exposure to PS-NP. A depiction of this method is shown in Figure 3.28.
For thin films (<100 nm) we observe that the elucidation of the irregularities is not prominent. Since the polystyrene nanoparticles are 40 nm in diameter, we believe there is a thickness threshold beyond which the particles are attracted to the surface and the method results in successful imaging of the defects. When we use thicker films (>100 nm) we observe that the irregularities are well elucidated under a fluorescence microscope, Figure 3.32. What was interesting, however, was the fact that the PS-NPs attach mainly to the edges of the created scratch. We attributed this effect to the fact that the nanoparticles adhere to the area where there is an enhanced contact between the substrate and the polymer.

As the films thickness increase, we observe that the fluorescence intensity of the edge definition also increases. The larger step’s height increases the contact area for the nanoparticles, which in effect lowers their entropy. In Figure 3.32, the step height is 350 nm as measured by AFM. The lower limit of this method success is dependent on the size
of the nanoparticle and film thickness, thus height of the edge. Based on our observation the edge height should be at least 1.5 times the particles diameter. Translating the method to thinner films would require using particles with smaller diameter.

Figure 3.29: Coated and scratched 2%, PS films exposed to PS nanoparticles for 10mins a) 90nm, b) 120nm

Figure 3.30: Coated and scratched 3%, 150nm PS film exposed to PS nanoparticles for 10mins. Scale bar represents 20µm
Figure 3.31: Coated and scratched 4%, 220nm PS film exposed to PS nanoparticles for 10mins. Scale bar represents 20µm

Figure 3.32: Coated and scratched 5%, 320nm PS film exposed to PS nanoparticles for 10mins. Scale bar represents 20µm
3.3 PATTERNED SUBSTRATES

As discussed previously the method worked very well in the case of random scratches and defects, we had one fundamental question to answer. The question was - what is the lowest possible defect size that could be measured using this method. In the CMP process where this research would find a significant practical application, it is clearly known that, when there is an error in the process, defects of various sizes and natures are created at once. Hence if the method elucidates a few defects within the damaged area, by varying the thickness of the polymer films, further failure analysis can be performed using higher resolution imaging methods such as SEM, TEM etc.

To pursue this study we obtained some patterned Si substrates from IBM Almaden Research Center. Dr. Ho-Cheol Kim was kind enough to provide some substrates with a multitude of patterns with a range of shape, size and length scales. We treated these patterned substrates with the method from section 3.2 and analyzed the substrates as to whether the nanoparticles clearly depicted the patterns. In this case the patterns are considered defects. From the images it was evident that the nanoparticles were deposited in the patterns coated regions selectively with appropriate polymer film thicknesses. These results brought us to the conclusion that the nanoparticle based detection of defects method could be translated to the patterned substrates detection as well. This is very useful and of practical importance because detection of pattern defects is in the same genre’ as defects in silicon wafer polishing steps.
Below we depict some of the patterns and select corresponding AFM images to elucidate the idea. In Figure 3.38, we use glass grit on the patterned substrate to create artificial defects in order to analyze the ensuing defects on the substrate. It is evident that the nanoprobe elucidates not only the pattern but also the defects on the substrate.

Figure 3.33: Patterned substrate where the nanoparticles elucidate the patterns clearly
Figure 3.34: Magnified picture of a pattern from the IBM substrate

Figure 3.35: AFM image of the pattern shown in Figure 3.
Figure 3.36: AFM image of the pattern spin coated with 3%, 170nm polymer film
Figure 3.37: Magnified picture of a pattern from the IBM substrate. The dark spots are irregularities in the film surface.

Figure 3.38: Fluorescence image of the patterned substrate where artificial defects were created using fine glass grit. The method is described in section 3.4.
Most images show random areas of NP adsorption where there is no underlying pattern defect i.e., “false positives”. These are regions of irregularities in the spun coat film surface. This has been dealt with in section 3.2.

3.4 COPPER COATED SI WAFERS

CMP involves mechanical and chemical grinding of the Si and/or Cu surfaces. One of the most important criteria for the application of this method in the CMP industry is the successful translation of this method onto Cu coated silicon substrates. We obtained Si substrates with Cu plated on them from NIST Polymers Division. We then used glass micro grit, P2500 (average particle diameter <8.4 microns), on the Cu substrates to create defects of various sizes and features, as also created a scratch on the Cu substrate as we did in the scratched Silicon substrate case. We then employed the nanoparticle based adsorption method to detect these defects on Cu coated substrates or simply referred to as “Cu substrates”. By varying the thickness of the film in order to find the ideal thickness as in the previous case, we found that this method works very well on Cu substrates.
Figure 3.39: Fluorescent image of PS nanospheres elucidating scratch and random defects on Cu substrate

The average roughness of the substrate was found to be around 70 nm and hence a coating of 175 nm thickness was used for the study to image the scratches and other defects with significant detail at multiple length scales as illustrated in Figure 3.39.
We want this method to be beneficial in defect detection at various stages of CMP process. We envision that the user will be able to check for defects at regular intervals or when the process parameters signify presence of defects. Our detection method requires coating of the substrate with specific polymer thin film, thus, in order to continue use of the substrate, the elimination of the polymer layer and nanoparticles is vital. Here, we propose few approaches and test one of them, namely dissolution of the coating.

Through use of various solvents, chloroform, toluene, ethanol, methanol, cyclohexane to dissolve the polymer layer, we determined that 10 minute-long sonication in toluene results in complete removal of PS film with dispersed nanoparticles. There is no visible disruption of the patterns on Si and Cu substrates as seen in Figure 3.41. Pictures of the substrate before and after sonication in toluene for the various substrates used in the previous sections are shown in .The AFM images are also shown as a reference along with the fluorescence images. For this study a blank patterned substrate was exposed to UVO for 15 minutes and dipped in a solution of nanoparticles. The nanoparticles adhere on the entire substrate, Figure 3.40, as discussed before. Figure 3.41 is the post sonication AFM of the substrate in Figure 3.34. AFM images clearly illustrate the difference between analyzed and sonicated-after substrates.
Figure 3.40: AFM image of plain Si wafer exposed to UVO for 15 minutes and later exposed to PS nanoparticles. The substrate was not coated with a thin film of polystyrene.
Figure 3.41: AFM image of the patterned substrate after sonication of Toluene for 10mins. Arrow indicates region of residual PS.

When dissolving the coating is not available, there are other methods that can be applied to remove the polymeric layer. If the substrates were plain silicon and had no copper, thermal degradation of PS film could be applied. The coated substrates should be annealed in the oven in air at 350°C to oxidize the PS layer, leaving substrates clear of any PS residue (Nowakowska, Kowal, & Waligora, 1978).
The results in this study fall into two criteria: substrates with defects and defects on the surfaces of thin films. The phenomenon between the two criteria, though similar in nature, has differences when it comes to their detection limits.

In the case of substrates with defects, which are discussed in section 3.1, 3.3 and 3.4, we gain the understanding that the nanoparticles are driven to the defects on the substrate only when the critical surface roughness to polymer thickness ratio is used. Enhanced contact area is responsible for the adsorption of the nanoparticles in the defects. The nanoparticles used in this study, QD’s and PS nanospheres carry an inherent negative charge. This results in the repulsion of like charged particles thus preventing agglomeration. Positively charged substrates would negate the idea behind the study by adsorption randomly on the substrate. Since we did not use any salts to the polymer solution, we assume that the polymer-coated substrates are neutral. Thus, the lack of adsorption of PS-NP and QDs to smooth areas of the PS coated substrate can be explained. Serizawa et al. (Serizawa et al., 2000, 1998) investigated the adsorption of
negatively charged PS nanoparticles on substrates coated with ultrathin polymer layers and observed that the adsorption proceeded faster and resulted in higher surface coverage when a higher salt concentration in the buffer was used. As expected, they observed no particle adsorption on surfaces bearing like signed charge as the particles. In studies performed by Antelmi et al. (Serizawa et al., 2000, 1998) on sapphire substrates and by Semmler et al. (Semmler et al., 1998) on mica substrates, the investigators observed that at the point of zero surface charge density, no particle adsorption was observed.

There are capillary forces influencing the nanoparticles that result from surface tension between the solvent and the particle material. Consequently, the evaporation of the solvent plays a critical role in structure formation of polymer layer. In addition, these capillary interactions will play role in: an application of a droplet of a particle suspension onto a substrate, during the controlled withdrawal of a sample from a particle suspension, during spin coating, and during an adsorption of particles to a substrate from a particle suspension (Antelmi & Spalla, 1999). As the thickness of the solvent layer became comparable to the particle diameter, attractive forces arise pulling particles together into the defects. Moreover, in the area of a scratch there is evident increase in contact area, compared to the defect free polymer thin film, which aids attraction forces and lead to nanoparticles adsorption.

In order to quantitatively analyze this data we took the same scratched Si wafer (Rq=125 nm) and coated with 1%, 2%, 3%, 4%, 5% wt. of PS and performed AFM studies. The studies were performed after the substrate was proven to adsorb the
nanoparticles onto the scratch at the 3% and 4% wt. of PS with varied spin speeds. We then measured the root mean square roughness of the coated area of the scratch and plotted the following graph.

![Graph](image-url)

**Figure 4.1**: Graph denoting thickness of the coated film vs. average roughness of the resulting scratched area

From the analysis of multiple scratches with varying roughness, we observe that the ideal ratio for the thickness of the thin film to the roughness of the underlying scratch is between 1-2. The ideal film thickness for the best fluorescence intensity would be around 1.5.

Adsorption of nanoparticles onto the substrates could also be explained through changes in their enthalpy and entropy. Coating the Si substrates with PS film reduces the enthalpic interactions and the nanoparticles are driven to the defects due to enhanced...
contact area and lowering entropy of the system. The selectivity to the defects in the case of Cu substrates makes it ideal for the method to be used in CMP process.

The question the end user might pose is the method employed when the initial size of the defect is unknown. In this case a cocktail of nanoparticles of varying sizes can be used for the detection of defects. The ideal scenario would be spin coating a random thickness of PS, lowest being 2 times the size of the smallest nanoparticle in the cocktail, onto the substrate and exposing it to the nanoparticle cocktail solution. Based on the sizes of the nanoparticles, the end user can change vary thickness until adsorption on the defects occurs. Regular use of this method would enhance the users understanding on the nature of defects, and a database of thickness with respect to the nature of the defects can be built and used as reference. In Figure 3.34, the substrate imaged has been analyzed using this method. We used a cocktail of nanoparticles ranging from 40 nm – 2.5 microns.

The method can also be used in an automated process where in the parameter of reference is the fluorescence intensity. An ideal wafer would have no fluorescence intensity due to the lack of defects where as a defect-ridden wafer would show significant fluorescence intensity.

Polymer films when deposited using various techniques like spin coating, drop casting etc. are not uniform. Non-uniformities arise due to various reasons such as, but not limited to, dust particles, incomplete dissolution of polymer that could act as a site for dewetting, solvent evaporation etc. The method depicted in section 3.2 could be used to
elucidate these defects. The disadvantage however would arise when the user would like to clean the substrate only of the nanoparticles. This would be rather difficult as the solvent generally used is toluene and it dissolves the polymer in question. Hence this approach could be used as a reference for thin films on substrates. It could be used to check for irregularities in the common method employed for a batch of substrates.
During the course of this study we believe we established basis for this new detection method. However, we acknowledge that the method has a significant undiscovered potential. Developing a method that identifies physical defects is what we have accomplished thus far. We believe that this method could be translated to detection of chemical patterns as well as their defects. Jason J. Benkoski from John Hopkins is working on detecting chemical patterns using amine coated quantum dots and has had significant success.

In this study we used a PS nanoparticle system along with a PS thin film. This method when used on plain Si wafers could be advantageous as the PS can be oxidized in air and removed in an oven at 320-350 °C. The heated wafer could be used immediately at that temperature for plasma enhanced chemical vapor deposition or other methods for depositing copper and dielectrics. But if there is a layer of copper already present, the temperature treatment would be a disadvantage and toluene needs to be used to remove the PS layer (F. Zhao et al., 2007).
We see a potential in creating a database of various polymer-nanoparticles systems that could be used for defect detection in corresponding substrates. In the introduction, Figure 1.1 shows the various materials being polished in various CMOS processes. The current system works for Cu substrates, Cu being the most widely used metal. If general users of the method had to use other metals, it would be convenient to have a database for reference on the polymer nanoparticle system for detecting the defects. Composing such a library would be a very important step, as it would open up the method to a wide range of metals and semiconductors.

In the semiconductor industry polyhydroxystyrene is used extensively as DUV resists and is etched out using standard etching procedures (McCoy, 2004). We propose that polyhydroxystyrene and corresponding nanoparticles could be used as the next system. This polymer can be etched out by standard etches without disturbing the soft copper layer (Petit & Moore, 2010).

During the course of the investigation on the irregularities in polymer thin film, and defects on the substrates, we observed that there were cases where the nanoparticles adsorbed on random areas on the substrates and resulted in false positives. In a way, surreptitiously, we were able to detect other surface imperfections, so that in fact these were not real false positives. The efficiency of the method due to the presence of these “false positives” proves that we can detect a wide range of defects sizes, which is a significant finding since during the course of CMP, the defects or scratched produced vary in size and shape.


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