Characterization of Optical Properties of Polyimide Precursors

作者：Dhiraj K. Sardar, Anthony Sayka*, and Raylon M. Yow

Abstract

Polyimide is considered to be a unique type of polymer possessing excellent mechanical, thermal, and chemical properties. It is an incredibly strong material and is resistant to both heat and to corrosive chemicals. When polyimide precursors cyclize to become the cured polymer, they form two distinct types of structures: linear and heterocyclic. Polyimides are widely used in the semiconductor industry as a dielectric material and stress reducing protective coating. Optical properties of polyimide precursors are investigated for their ability not to adversely affect target recognition by a HeNe laser beam.

* Current Address: Maxim Integrated Products, San Antonio, Texas 78251

INTRODUCTION

In recent years, the use of photosensitive polyimides has greatly increased in the semiconductor industry owing to the compatibility of their thermal and dielectric characteristics with semiconductor device requirements. Polyimides are used in the semiconductor industry primarily as a protective coating material for semiconductor devices. In the conventional application of polyimide, a thick film of photosensitive polyimide is spun on a wafer using a dispense technique similar to a photoresist process. Typically, a coated wafer is soft baked to evaporate the majority of the solvents contained in the polyimide precursor mixture. Subsequently, the wafer is exposed and developed. The patterned wafer is then hard baked before going to final cure. Cured polymer is fully formed at that point.

It has been suggested that a photosensitive polyimide requires significantly reduced process time and offers superior results compared with nonphotosensitive polyimide.[1] Therefore, photosensitive polyimide has become the natural choice for the semiconductor industry for many years.

Absorption of light by photosensitive polyimide can be a critical factor to consider when setting up a photolithographic process. The Beer's law of absorption can be used to calculate the change in light intensity within the photosensitive polyimide.[2] Due to the complex nature of photosensitive polyimide, both absorption and scattering should be considered when evaluating optical properties of photosensitive polyimide. UV light is routinely employed in the photolithographic process. It is expected that photosensitive polyimide will strongly absorb UV light, while absorption of the longer wavelength visible light is expected to be significantly smaller. This is an important consideration since visible light (632.8 nm) from a HeNe laser is used for target recognition and alignment of stepper-aligned wafers. A photo of a typical alignment target on a semiconductor wafer is shown in Fig. 1.

In this paper, we characterize the optical properties of a positive photosensitive polyimide precursor mixture. The optical properties investigated include index of refraction and absorption coefficient at HeNe laser wavelength (632.8 nm).

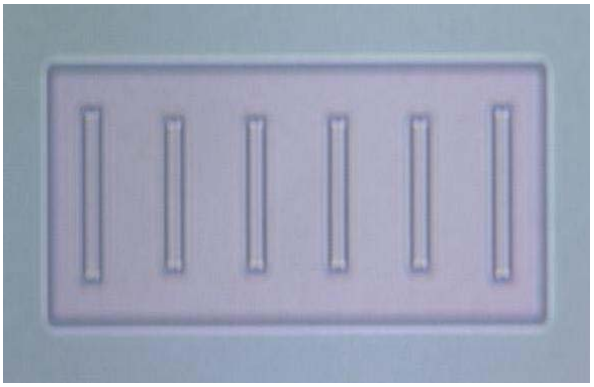

Fig. 1. Photo of a typical alignment target on a semiconductor wafer.

MATERIALS AND METHODS

The polyimide precursor sample used in this study was obtained from Fujifilm Electronic Materials, Inc., North Kingstown, RI. The product name is AP2210A. It consists of gamma-butyrolactone (55-75%), polyamide (20-40%), naphthoquinone ester derivative (2-6%), alkoxy silane (1-3%), and aryl silicic acid (0.5-2%).

Preparation of the polyimide precursor sample for the optical measurements involved fixing an O-ring with a diameter of 1.0 inch between two glass slides; the O-ring acts as a reservoir to retain the liquid sample. The polyimide precursor mixture was then transferred with a pipette into the reservoir for investigation. The sample thickness in this case was the thickness between the glass slides and was measured to be 0.1 cm.

OPTICAL MEASUREMENTS

Measurement of absorption spectrum

The room temperature absorption spectrum of the polyimide precursor sample was measured from 525 to 800 nm using a Cary-14 spectrophotometer modified by OLIS. Before taking the absorption spectrum on this sample, a base line was set to correct the measured spectrum due to Fresnel reflection losses of about 5% and any marginal wavelength-dependent scattering that might occur. The absorption spectrum was corrected for those losses by subtracting the base line from the measured data.

Measurement of index of refraction

The index of refraction of the polyimide precursor solution was measured at 654 nm using a Michelson interferometer. The experimental set-up is shown in Fig. 2. This method was chosen for its simplicity and accuracy.

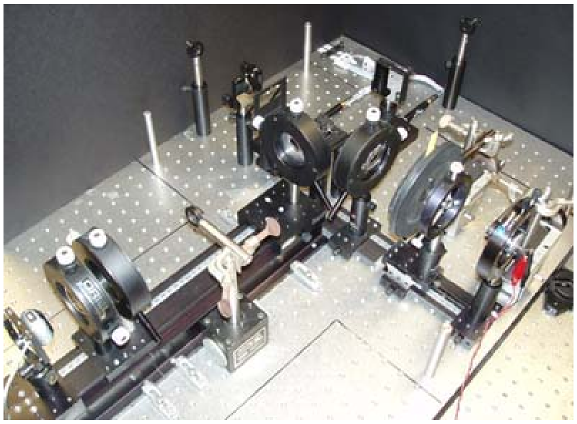

Fig. 2. Experimental set-up for Michelson Interferometer to measure index of refraction.

Measurement of total diffuse reflectance and total diffuse transmittance

The total diffuse reflectance and total diffuse transmittance measurements were taken using a single integrating sphere (Oriel model 71400). The polyimide precursor sample was placed in a specially designed holder that was mounted to one of the ports of the integrating sphere. The light source used for these measurements was a HeNe laser (model LHRP-0501 from Electro-Optics). The average output power of the laser was 5 mW, the beam diameter at $1/e^2$ was 0.8 mm, and the beam divergence was 1.01 mrad at 632.8 nm.

The schematic of the experimental set-up employed to measure the total diffuse reflectance and total diffuse transmittance is similar to that used in reference 2, and is shown in Fig. 3. The laser was directed into the entrance port A of the integrating sphere, whose exit port B is either open or capped with a reflective surface identical to that of the interior surface of the integrating sphere depending on the measurement taken. The diameter of the sphere was 6.0 inch and each port had a diameter of 1.0 inch. Light leaving the sample was reflected multiple times off the inner surfaces of the sphere. A reflecting baffle within the sphere shielded the photomultiplier tube (PMT) from direct emission from the sample. Port A was equipped with a variable aperture so that the beam diameter could be appropriately controlled. The reflected and transmitted light intensities were detected by the PMT (Oriel model 7068) attached to the measuring port. The PMT was powered by a high voltage power supply (Bertran, model 215). The signal from the PMT was sent to a digital multimeter (Emco, DMR-2322). The measured light intensities were then utilized to determine the total diffuse reflectance R_d and total diffuse transmittance T_d by the following formulas:

$$R_d = \frac{X_r - Y}{Z - Y} \qquad (1)$$

and

$$T_d = \frac{X_t - Y}{Z - Y} \qquad (2)$$

where X_r is the intensity detected by the PMT with the sample at B, X_t is the intensity detected by the PMT with the sample at A and Z is the intensity detected by the PMT with no sample at A and a reflective surface at B, and Y is the correction factor measured by the PMT with neither a sample at A nor a reflective surface at B.

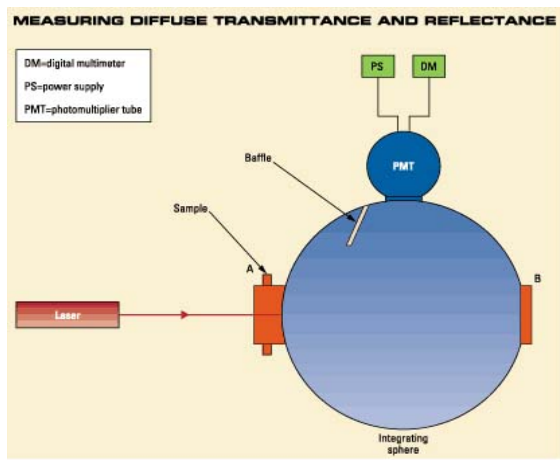

Fig. 3. The experimental set-up used to measure the total diffuse transmittance (T_d) and total diffuse reflectance (R_d) used an integrating sphere. The laser was directed into the entrance port A of the integrating sphere, whose exit port is either open or capped with a reflective surface identical to that of the interior surface of the integrating sphere depending on the measurement taken.

An attempt was made to measure total diffuse reflectance and total diffuse transmittance on the polyimide precursor sample at 632.8 nm using an integrating sphere. However, the diffuse reflectance at this wavelength was too small to measure accurately. Therefore, the Inverse Adding Doubling (IAD)[3] method could not be applied to this particular material, and hence no data was obtained for the scattering of light at the HeNe wavelength.

RESULTS AND DISCUSSION

The room temperature absorption spectrum was taken on the polyimide sample between 525 and 800 nm on the Cary-14 spectrophotometer, and is shown in Fig. 4. The spectrum clearly shows that the absorbance of the polyimide precursor sample is extremely high in the wavelength region below 550 nm, while it is significantly less in the wavelength range above 600 nm. The absorption spectrum in Fig. 4 indicates that the absorption for the polyimide sample is significantly low at 632.8 nm, the HeNe laser output wavelength. Using Beer's exponential decay law, the absorption coefficient at 632.8 nm was determined to be approximately 8.0 cm^{-1}.

It is important to note that due to the intrinsic transparent nature of polyimide at 632.8 nm, we were unable to obtain a reflectance measurement at this wavelength. This suggests that polyimide has negligible scattering and is the primary reason that the IAD method could not be applied in our study.

The index of refraction of the polyimide precursor sample was measured at 654 nm and found to be 1.54. The refractive index at 632.8 nm can be assumed to be close to this value owing to the small variation in the dispersion curves for most materials at wavelengths above 600 nm.[4]

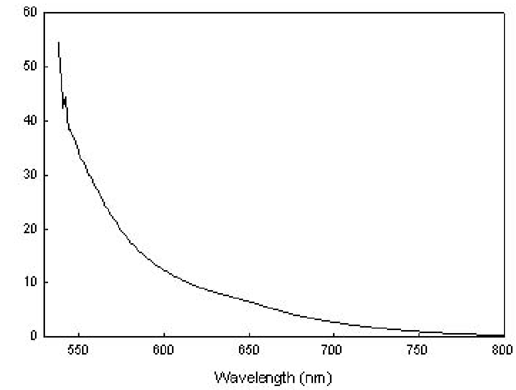

Fig. 4. Absorption spectrum of the polyimide sample at room temperature.

CONCLUSIONS

A rapid increase in the use of photosensitive polyimides has been seen in recent years in the semiconductor industry mainly because of their excellent thermal and dielectric properties which are compatible with the industry's requirements. Photosensitive polyimides are mainly used for interlevel insulation and stress buffer. However, among the applications of polyimide, the stress buffer is by far the most important one.

Values of the optical properties of a photosensitive polyimide precursor mixture reported in this paper are of significant importance to the semiconductor industry. An in-depth knowledge of optical properties of polyimide is imperative for semiconductor wafer manufacturers and process engineers to be able to successfully assess optimal target recognition. Our study indicates that absorption at 632.8 nm by a polyimide precursor solution is low, and scattering at this wavelength is too small to measure. Therefore, a coating of polyimide is not expected to adversely affect target recognition using a HeNe laser beam.

Acknowledgement

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Author information

Dhiraj K. Sardar is a professor of physics at the University of Texas at San Antonio. He has more than 25 years of research experience in laser materials, and has supervised a large number of student research projects involving characterization of optical and laser properties of various solid-state laser materials. He received a Ph.D. degree in Physics from Oklahoma State University.
Phone: 1-210-458-5748
E-mail: dsardar@utsa.edu

Anthony Sayka received an M.B.A. degree and a B.S. degree in Physics from the University of Texas at San Antonio and is currently employed by Maxim Integrated Products, Inc. He has 15 years of experience in the semiconductor industry, including engineering positions with Intel, Advanced Micro Devices, VLSI Technology Inc., and Micron Technology Inc. He also has a B.S. degree in Chemistry from the University of Colorado at Colorado Springs. He has published seven papers in the areas of semiconductor processing and laser materials, and holds numerous patents.
E-mail: saykacr@hotmail.com

Raylon M. Yow received a B.S. degree in Mechanical Engineering and a M.S. degree in Mathematics from the University of Texas at San Antonio and a M.S. degree in Mechanical Engineering from the University of Texas at Austin. He has ten years of research experience in laser spectroscopy and semiconductor materials. He has published fourteen papers on optical characterization of semiconductor and laser materials.