Thermal conductivity measurements of thin-film resist

Dachen Chu[a)]
Solid State and Photonics Laboratory, Center for Integrated Systems, Stanford University, Stanford, California 94305-4075

Maxat Touzelbaev and Kenneth E. Goodson
Mechanical Engineering Department, Stanford University, Stanford, California 94305

Sergey Babin[b)]
Etec Systems

R. Fabian Pease
Solid State and Photonics Laboratory, Center for Integrated Systems, Stanford University, Stanford, California 94305-4075

(Received 15 June 2001; accepted 8 October 2001)

In electron-beam and photolithography, local heating can change the resist sensitivity and lead to variations in significant critical dimension. Existing models suffer from the lack of experimental data for the thermal properties of the polymer resist films. We present the measurements of both out-of-plane and in-plane thermal conductivity of thin resist films following different exposure conditions. An optical thermoreflectance technique was used to characterize out-of-plane thermal conductivity; the out-of-plane thermal conductivity of exposed SPR™-700 resist increases as a function of exposure dose. We also designed and fabricated a free-standing micro-electrode structure for measuring the in-plane thermal conductivity and results for poly(methylmethacrylate) films were obtained, indicating that, unlike polyimide films, there is no appreciable anisotropic behavior. [DOI: 10.1116/1.1421557]

I. INTRODUCTION

With the exception of wafer direct writing, all advanced lithography demands photomasks with stringent tolerance as critical dimensions (CDs). These masks are typically fabricated using electron-beam exposure of resist films on chromium-on-quartz substrates. To meet the Semiconductor International Association (SIA) Roadmap requirements, higher beam voltage and higher beam currents are being used leading to increased power density (1 GW/c.c. or higher) and this can cause resist local heating. The local heating can change the resist sensitivity and lead to significant variations in CD.[1,2] To model such heating satisfactorily we need to know the thermal properties of the resist films. One well-known resist, poly(methylmethacrylate), (PMMA), has been characterized in terms of its thermal conductivity using different techniques,[3,4] but data are scarce for other resists, and most previous work was confined to characterizing the unexposed resist. Because the molecular structure of the resist changes on electron exposure, the thermal properties can also change. Prior work in our group also indicated that certain polymers, for example, polyimide, have strong anisotropic thermal conductivity.[5] So both out-of-plane and in-plane thermal conductivity have to be characterized on resists thin films.

Here, we describe measurements of thermal conductivity both normal to (''out-of-plane''), and in the plane of, the resist film. Out-of-plane thermal conductivity was measured using noncontact thermoreflectance thermometry.[6] For in-plane measurements, we designed and fabricated a free-standing micro-electrode structure and we obtained results for PMMA.

II. OUT-OF-PLANE MEASUREMENTS

A. Experimental method

We used a noncontact thermo-reflectance technique to measure the out-of-plane thermal conductivity of the resist thin film. As shown in Fig. 1, two laser beams impinge on the surface of the measured sample. One, the pump, a Nd:YAG laser with a 6 ns pulse and 10 Hz repetition frequency, generates a transient vertical heat flux on the metallized sample. The surface temperature decay was determined by monitoring the optical reflectivity (at 633 nm) (Fig. 2). The probe beam is coupled into an optical microscope and is focused to a diameter much less than 1 mm to increase sensitivity, while the pump laser has a diameter of about 1 mm (much greater than the film thickness) to ensure one-dimensional heat conduction. The polarization cube was used to regulate the optics and to prevent the reflected light from being coupled into the probe laser cavity. A band pass filter prevented the pump laser radiation from leaking into a PIN photodetector. Then, the signal is amplified and collected by a digitizing oscilloscope (Tektronix DSA-600). Finally, we extracted the out-of-plane thermal conductivity of resist film from the shape of the time-decaying temperature profile as analyzed by a personal computer.

The sample preparation included spin coating the resist and depositing a 400-nm-thick aluminum layer on top of the

[a)]Electronic mail: dcchu@stanford.edu
[b)]Presently at: Soft Services Incorporated, 5286 Dunnigan Ct., Castro-Valley, CA 94546.

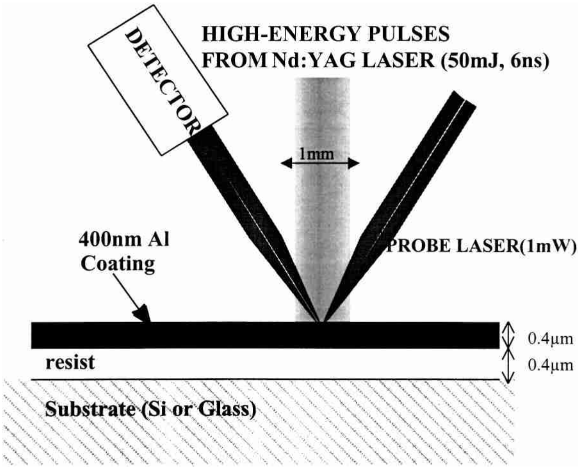

FIG. 1. Thermoreflectance method for determining the out-of-plane thermal conductivity of resist. Monitoring the reflectivity of the metal film allows us to follow the decay of surface temperature when we can determine the thermal conductivity of resist.

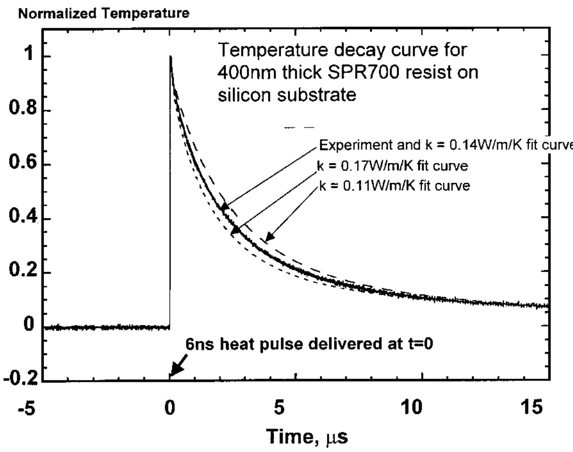

FIG. 3. Experimental temperature decay curve (from the experiments of unexposed SPR-700 resist) and corresponding curve fit of solution to heat conduction equation for the three different values of thermal conductivity k, clearly $k = 0.14$ W/m/K is the best fit of 400-nm-thick unexposed SPR-700 resist thin film on silicon substrate.

resist. The aluminum was deposited slowly (a few angstroms per second) to avoid distorting the resist. To measure the thermal conductivity as function of exposure dose, some samples are exposed before metallization. The exposure tool is a variably shaped EBL system with 50 kV beam voltage and 10 A/cm^2 beam current density. We exposed a series of 5 mm squares on one wafer with different doses (5, 10, 20, 40, 80, and 160 $\mu C/cm^2$). Multiple pass (5 $\mu C/cm^2$ per shot) exposures were applied to avoid over heating. We also checked that the thickness of resist is unchanged after exposure.

We used very short time scale (μs) in the measurement, so that the shape of temperature decay is strongly influenced by the thermal conduction in the metal-resist structure. The measured shape of the decay of surface temperature is interpreted by solving the one-dimensional heat conduction equation in the frequency domain:

$$\frac{i \times \omega}{\alpha_n} \theta_n = \frac{d^2 \theta_n}{d z_n^2}.$$

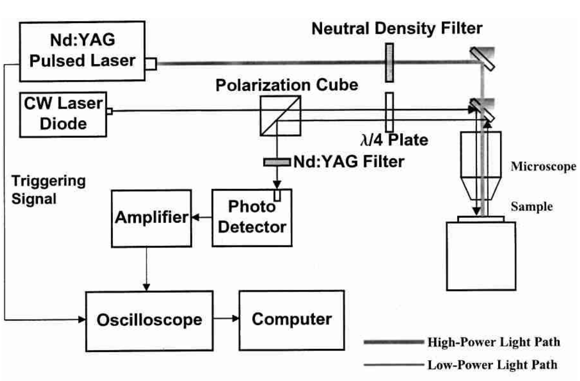

FIG. 2. Schematic of experiments for determining out-of-plane thermal conductivity.

Ideal thermal contact boundary conditions are assumed, i.e., $k_n d\theta_n / dz_n$ and θ_n are continuous at the interface; θ_n, k_n and α_n are the temperature, thermal conductivity, and diffusivity respectively, in the nth layer, and z_n represents the direction normal to the multilayer structure. The temperature decay is dominated by the heat capacity of the metal layer (we used the Al bulk value[7] at room temperature 2.32×10^6 $J/W/m^3$) and by the thermal conductivity of the resist layer.

B. Results and discussion

The decay of temperature of a SPR resist film is fitted with the three different values of resist conductivity (Fig. 3). The systematic errors were estimated to be within 20%, caused primarily by the uncertainty of film thickness and by noise.

The results for PMMA, UVII-HS, ZEP-7000, and SPR-700 are listed in Table I. The PMMA value agrees well with previous results.[3,4] We also measured the out-of-plane thermal conductivity for SPR-700 resist as a function of prior exposure dose. The results are shown in Fig. 4, where each point represents the average of five measurements; the standard deviations of the five measurements are less than 5% of the mean value. The error bars represent the error sources discussed in the last paragraph. From Fig. 4, we see that the thermal conductivity increases with the exposure dose until

TABLE I. Out-of-plane thermal conductivity of various unexposed resist.

Resist	Substrate	Thickness (nm)	Thermal conductivity (W/m/k)
SPR-700	Silicon	400	0.14 ± 0.03
PMMA	Silicon	400	0.16 ± 0.03
ZEP-7000	Silicon	400	0.16 ± 0.03
UVII-HS	Silicon	400	0.19 ± 0.03

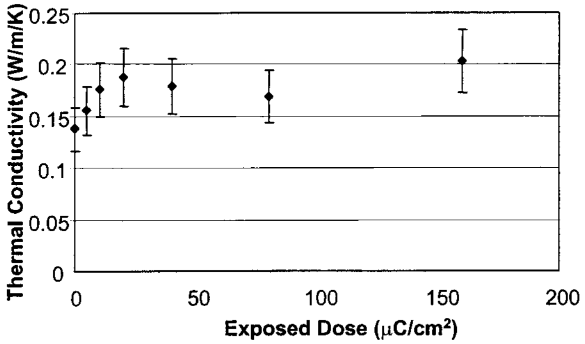

FIG. 4. Out-of-plane thermal conductivity of SPR resist following a variety of doses.

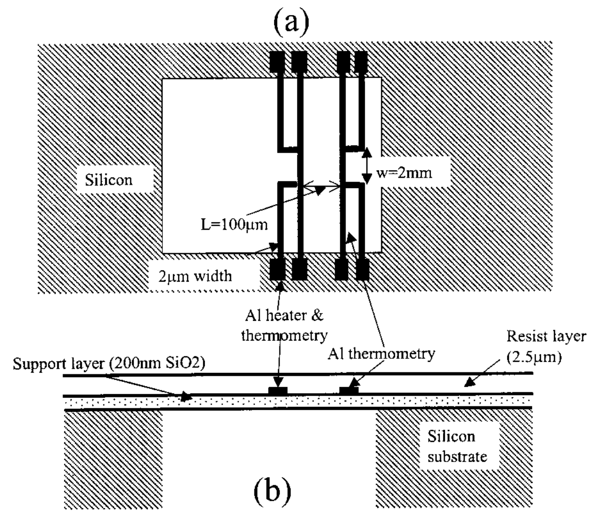

FIG. 5. (a) Top view and (b) cross section view of the structure for determining in-plane thermal conductivity.

the dose reached 40 μC/cm^2 (the nominal required dose). At higher doses, there is no further increase in thermal conductivity.

The primary impact of electron irradiation on SPR700 is to convert the photoactive compound from a diazonapthaquinone to an indene carboxylic acid. This chemical conversion changes the infrared vibration spectra of the resist and hence it might increase the phonon velocity and mean free path as well. It can lead to higher conductivity according to the following relationship:[8]

$$k=\tfrac{1}{3}C_V v l,$$

where C_V is the heat capacity, v is the phonon transport velocity and l is the phonon mean free path. While this equation is not strictly valid for highly disordered materials including polymers owing to the strong scattering of phonons, the equation provides some insight into the qualitative relationship between the thermal conductivity, the heat capacity, the acoustic velocity, and phonon mean free path. Other factors that could also account for this increase include a change in density (which would affect C_p in the latter equation) and a change in the elastic constant due to the changes in resist glass transition temperature caused by the formation of the indene carboxylic acid.

Whatever the physical basis for the experimental result that upon exposure, the thermal conductivity of SPR-700 increasing by up to 40% raises the suspicion that the previously predicted values of temperature rise, based on the value of thermal conductivity before exposure, might have been significantly overestimated.

III. IN-PLANE THERMAL CONDUCTIVITY MEASUREMENT

Free-standing membrane structures were fabricated to measure in-plane thermal conductivity using steady state ohmic heating and monitoring the temperature sensitive resistance of the microelectrodes (Fig. 5). The double-layer membrane window is $0.5\,\mathrm{mm}\times 10\,\mathrm{mm}$, and the top layer is the resist film to be measured. Between the two layers are two aluminum microbridges 2 μm wide and 200 nm thick which can be used as both heaters and electrical resistance thermometry. With electrical current through the aluminum bridge located in the center of free-standing membrane, heat is generated and diffuses along the membrane and the resistances of the electrodes are monitored. The structure is designed such that the length of the aluminum bridge (2 mm) is much larger than the distance between two Al bridges (0.1 mm) and the thickness of the membrane ($\sim$3 μm), heat flux is one dimensionally conducted from the center bridge to the side. According to Fourier's law, we can determine the thermal resistance:

$$R_{\mathrm{thermal}}=\frac{T_1-T_2}{P/2},$$

where T_1 and T_2 stand for the temperatures of aluminum bridges in the center and edge of membrane, P is the power generated in the heater bridge.

For this double layer membrane, the measured thermal resistance is the parallel of the resistance of the resist membrane and the supporting membrane.

$$\frac{1}{R_{\mathrm{total}}}=\frac{(k_{\mathrm{resist}}\times d_{\mathrm{resist}}+k_{\mathrm{support}}\times d_{\mathrm{support}})\times w}{L},$$

where k is the thermal conductivity, d is the thickness of the membrane, w is the length of aluminum bridge, 2 mm, and L is the distance between the two bridges, 100 μm.

The ideal structure for resist thermal conductivity measurement would be a free-standing resist membrane without the supporting layer, but unfortunately, it could not be practically fabricated with our techniques. Therefore, in order to get thermal conductivity of resist, we also measured the thermal resistance of the supporting layer by etching the resist layer off the sample. Thermal resistance of the supporting layer is

$$\frac{1}{R_{\mathrm{support}}}=\frac{k_{\mathrm{support}}d_{\mathrm{support}}w}{L}.$$

By subtracting $1/R_{\mathrm{support}}$ off $1/R_{\mathrm{total}}$, we can get the value of thermal conductivity of the resist. To eliminate the measurement uncertainty, a high value of figure of merit $\beta = k_{\mathrm{resist}} d_{\mathrm{resist}} / k_{\mathrm{support}} d_{\mathrm{support}}$ is desired. However, difficulty comes from the fact that the thermal conductivity of resist is approximately an order of magnitude smaller than usual supporting membrane such as silicon dioxide or silicon nitride. These materials should also function as the etch stop material for silicon when we etched the bulk silicon to build free-standing membrane. In order to get a high β, we chose very thin film (200 nm) of silicon dioxide (we measured $k = 1.2$ W/m/K) as a supporting layer, and spin coated 0.8 μm thick PMMA film three folds, to obtain a total resist thickness of 2.5 μm. With this structure, a lateral thermal conductivity value 0.16 W/m/K of PMMA was obtained. The errors in the measurements came from thermometry calibration, radiation heat loss, and uncertainty in membrane thickness. We estimated that they are less than 5%, 5%, and 10% correspondingly, leading a total error less than 15%. Within this uncertainty range, the in-plane value is consistent with previous research[3,4] and we can conclude that the thick PMMA (0.8 μm) has isotropic behavior in thermal conductivity, but a smaller value compared with the bulk value, 0.21 W/m/K.[9]

IV. SUMMARY AND CONCLUSIONS

Two techniques for measuring the thermal conductivity of thin polymeric films have been described. Both in-plane and out-of-plane thermal conductivity of resists were measured and preliminary results were obtained. The out-of-plane thermal conductivity of SPR-700 resist increases significantly upon electron-beam exposure, which is possibly due to the material structure change of polymeric resist. In-plane thermal conductivity results for PMMA films indicate that, unlike earlier results for polyimide, there is no appreciable anisotropy; but the thin-film values are only about two-thirds of the bulk value. Thus, it appears that to have meaningful values for the thermal conductivity of thin polymeric films, we must directly measure values under the relevant conditions.

ACKNOWLEDGMENTS

This work was sponsored by Semiconductor Research Corporation under Contract No. MJ-653 and Intel Ltd. Thanks are owed to Dr. Katsuo Kurabayashi and Dr. Peng Zhou for stimulating discussions and technical expertise, and to the Mask Advisory Group for their suggestions and encouragements.

[1]T. R. Groves, J. Vac. Sci. Technol. B **14**, 3839 (1996).
[2]S. Babin and I. Y. Kuzmin, J. Vac. Sci. Technol. B **16**, 3241 (1998).
[3]D. Cahill and R. O. Pohl, Phys. Rev. B **35**, 4067 (1987).
[4]S. Govorkov, W. Ruderman, M. W. Horn, R. B. Goodman, and M. Rothschild, Rev. Sci. Instrum. **68**, 3828 (1997).
[5]K. Kurabayashi and K. E. Goodson, J. Appl. Phys. **86**, 1925 (1998).
[6]K. E. Goodson, J. Appl. Phys. **77**, 1385 (1995).
[7]Y. S. Touloukian and E. H. Buyco, *Thermophysical Properties of Matter* (IFI/Plenum, New York, 1970), Vol. 1, pp. 1–9.
[8]C. L. Choy, Polymer **18**, 984 (1977).
[9]*Physical Properties of Polymer Handbook* (1996), pp. 111–118.