APPLIED PHYSICS LETTERS **88**, 153121 (2006)

Femtosecond-laser-induced delamination and blister formation in thermal oxide films on silicon (100)

Joel P. McDonald,[a] Vanita R. Mistry, Katherine E. Ray, and Steven M. Yalisove
Department of Materials Science and Engineering and Center for Ultrafast Optical Science, University of Michigan, 2300 Hayward Street, Ann Arbor, Michigan 48109-2136

John A. Nees
Center for Ultrafast Optical Science, University of Michigan, 1006 Gerstacker Building, 2200 Bonisteel Avenue, Ann Arbor, Michigan 48109

Neville R. Moody
Sandia National Laboratories, P.O. Box 969 MS9409, Livermore, California 94551-0969

(Received 11 January 2006; accepted 13 March 2006; published online 13 April 2006)

Silicon (100) substrates with thermal oxide films of varying thickness were irradiated with single and multiple 150 fs laser pulses at normal and non-normal incidences. A range of laser fluence was found in which a blister or domelike feature was produced where the oxide film was delaminated from the substrate. At normal and non-normal incidences blister features were observed for samples with 54, 147, and 1200 nm of thermal oxide. The blister features were analyzed with optical and atomic force microscopy. In addition, the time frame for blister growth was obtained using pump-probe imaging techniques. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2193777]

Silicon (Refs. 1–7) and SiO_2 (Refs. 8–10) have been popular material choices for femtosecond laser damage studies over the past several years. Significant knowledge of the electrical and mechanical properties of these materials has been gained from other fields, thus making silicon and SiO_2 preferred testing grounds upon which to study the unique damage and modification produced by ultrashort laser pulses. In this work, we report on interesting phenomena resulting from the interaction between femtosecond laser pulses and Si (100) with thermal oxide films of varying thickness at normal and grazing laser incidence. Similar blistering phenomena have been observed with 0.9 ns pulsed laser irradiation at normal incidence of thermal oxide films (25–100 nm in thickness) on Si substrates,[11,12] and in 300 nm aluminum films on glass substrates irradiated with nanosecond laser pulses.[13] The results presented here suggest that the mechanism leading to the blistering phenomenon is quite different from those earlier results using laser pulses of temporal width exceeding hundreds of picoseconds.

Si (100) wafers with 20, 54, 147, and 1200 nm thick thermally grown oxide (SiO_2) films (thickness determined via ellipsometry) were used in this study. During exposure to the laser beam, sample position was controlled using a four axis motorized translation stage. The laser used was a commercially available amplified Ti:sapphire laser, operating at a wavelength of 775 nm and a repetition rate of 125 Hz, producing pulses with an energy of 720 μJ and temporal pulse width of 150 fs. Laser pulses were directed onto the sample at 0° and ~77.4° with respect to the sample normal. Both *s*- and *p*-polarized laser pulses were used at the non-normal laser beam incidence.

After irradiation of Si (100) with thermal oxide films with femtosecond laser pulses, a bubble or blister feature has been observed resulting from the delamination and subsequent vertical expansion of the film upward from the substrate. In Fig. 1, optical microscope (OM) images of blisters produced at normal and grazing incidences are presented. The blister phenomenon was observed for thermal oxide films of 54, 147, and 1200 nm thicknesses with the laser beam incident at normal and grazing incidences.

Atomic force microscopy (AFM) section analyses of blisters produced on Si (100) with 1200 nm of thermal oxide at normal incidence are presented in Fig. 2, while AFM of blisters produced with multiple laser pulses at grazing incidence is presented in Fig. 3. The height and width of the blisters were found to depend on the laser fluence, laser

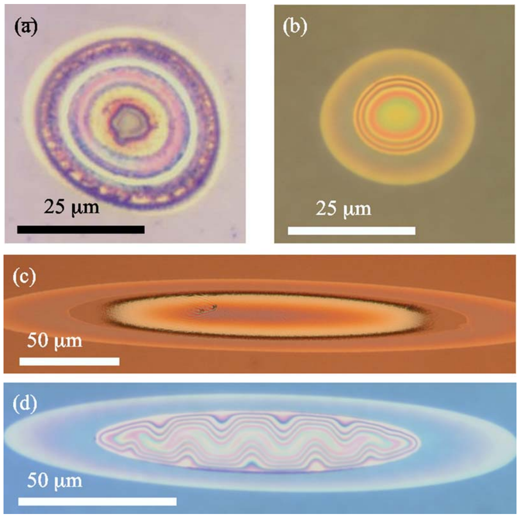

FIG. 1. (Color online) OM images of blister features produced on Si (100) with thermal oxide films using single 150 fs laser pulses. Interference fringes present in images are due to constructive interference through optical spectrum as height of blister changes. (a) Normal incidence: 1200 nm thermal oxide; laser fluence=0.69 J/cm^2. (b) Normal incidence; 147 nm thermal oxide; laser fluence=0.33 J/cm^2. (c) Grazing incidence: 1200 nm thermal oxide: laser fluence=0.3 J/cm^2; *s*-polarized laser pulse. (d) Grazing incidence: 147 nm thermal oxide; laser fluence=0.58 J/cm^2; *p*-polarized laser pulse.

---

[a] Author to whom correspondence should be addressed; electronic mail: jpmcdona@umich.edu

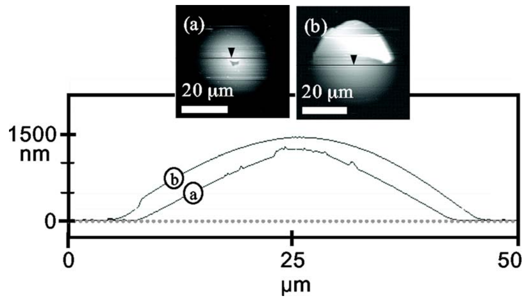

FIG. 2. (Color online) AFM section analysis of blister features produced on Si (100) with 1200 nm of thermal oxide with single 150 fs laser pulses at normal incidence. Inset AFM images show locations of section scans across blisters presented in the plot. (a) Laser fluence=0.69 J/cm^2, max height=1250 nm, and width=36 μm. (b) Laser fluence=0.86 J/cm^2, max height=1460 nm, and width=40 μm. Slight blister popping is apparent in the image.

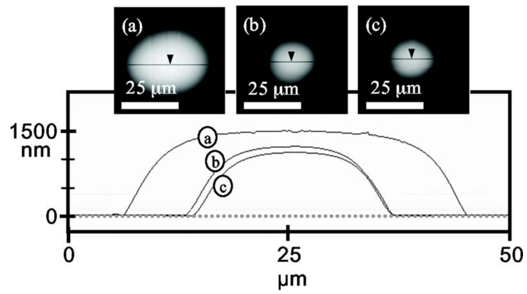

FIG. 4. (Color online) AFM section analysis of blister features produced on Si (100) with 147 nm of thermal oxide with single 150 fs laser pulses at normal incidence. Inset AFM images show location of section scans presented in the plot. (a) Laser fluence=0.40 J/cm^2, max height=1510 nm, and width=39 μm. (b) Laser fluence=0.33 J/cm^2, max height=1223 nm, and width=23 μm. (c) Laser fluence=0.30 J/cm^2, max height=1126 nm, and width=23 μm.

beam angle of incidence, and number of laser pulses used to make the feature.

AFM section analyses of blisters produced on Si (100) with 147 nm of thermal oxide at normal incidence are presented in Fig. 4, and for grazing incidence in Fig. 5. The wavy nature of the blister produced at grazing incidence for the sample with 147 nm of thermal oxide is a characteristic of the telephone cord instability commonly observed for thin film delamination of a compressively stressed film.[13,14] The wavy nature is absent in the blisters produced on samples with 1200 nm of thermal oxide.

A pump-probe imaging technique was employed to characterize the temporal evolution of blister growth. With this technique, a primary pump pulse (at a wavelength of 780 nm) is used to initiate blister growth, while an image is formed with the reflection of a time delayed probe pulse (at a wavelength of 390 nm) from the sample surface excited by the pump pulse. Once blister growth ensues, these images display the presence of an interference phenomenon known as Newton's rings, the temporal evolution of which can be used to determine the expansion rate of the blister from the substrate.[15] Images showing the presence of the Newton's rings are shown in Fig. 6. Blister expansion is assumed to begin at some time prior to the observation of the first interference minimum in the captured image. The first such interference minimum for a blister generated in a 54 nm thermal oxide film occurred at a probe time delay of 1.6 ns, while the images of a blister formed in a 1200 nm film showed the first interference minimum at 8.35 ns (laser fluence in each case was 0.8 J/cm^2). This suggests two things: first that the thickness of the film plays a critical role in blister formation dynamics, and second, that the laser induced blister formation takes place on time scale of hundred of picoseconds to nanoseconds. As such, a blister formed using a femtosecond laser pulse is created under qualitatively different conditions than a blister produced with a longer, nanosecond pulsed laser, as the energy from a femtosecond laser pulse is completely deposited before physical changes to the material structure occur.[16]

A physical model consistent with the observation of blister generation in thermal oxide films on Si (100) substrates must first consider the location at which the laser energy is absorbed by the sample. SiO_2 is largely transparent at the laser wavelength and fluence used in this study; 780 nm and less than 1 J/cm^2, respectively. As such the incident laser pulse is expected to pass through the thermal oxide film without depositing significant energy into the film, and instead deposits its energy into the Si (100) substrate where the laser energy is initially absorbed by the valence electrons. At sufficient laser intensities, the electrons are stripped from their host atoms producing a high density electron-hole plasma, and breakdown of the substrate ensues as these electrons transfer their energy to the lattice.[16] The breakdown of the substrate results in the delamination of the thermal oxide

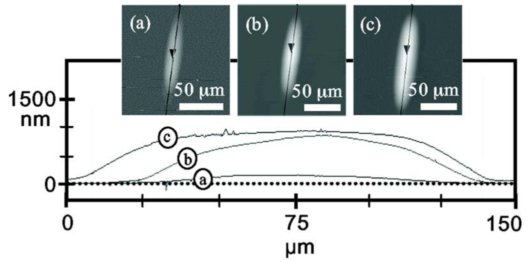

FIG. 3. (Color online) AFM section analysis of blister features produced at grazing incidence (77.4° to sample normal) on Si (100) with 1200 nm of thermal oxide with multiple 150 fs laser pulses. The laser fluence was 0.47 J/cm^2 with the laser beam p-polarized with respect to the sample. Inset AFM images show location of line scans presented in the plot. (a) Blister feature made with three laser pulses, max height=143 nm, and width =20 μm; (b) five laser pulses, max height=864 nm, and width=29 μm; (c) ten laser pulses, max height=892 nm, and width=33 μm.

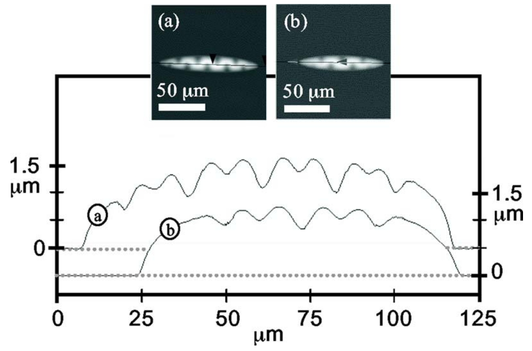

FIG. 5. (Color online) AFM section analysis of blister features produced on Si (100) with 147 nm of thermal oxide with single 150 fs laser pulses at grazing incidence (~77.4° to sample normal). The laser was p polarized with respect to the sample surface. Inset AFM images show locations of cross sections presented in plot. Cross sections have been offset for clarity. (a) Laser fluence=0.58 J/cm^2, max height=1705 nm, and width=21 μm. (b) Laser fluence=0.47 J/cm^2, max height=1302 nm, and width=15 μm.

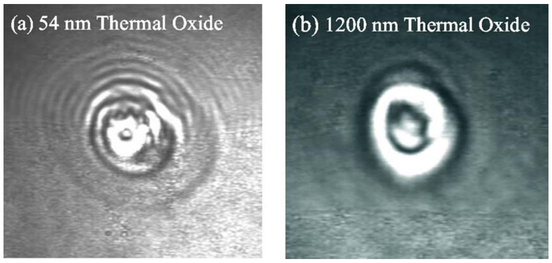

FIG. 6. (Color online) Snap-shot images collected of bubbles at 11.03 ns after initiation of blister growth using pump-probe imaging technique. The laser fluence of the pump pulse was 0.8 J/cm^2 in both images, resulting in the formation of a blister in the film: (a) 54 nm thermal oxide film; (b) 1200 nm thermal oxide film.

film. It has been suggested that near the threshold for femtosecond laser induced damage, the breakdown of material is first accompanied by the formation of a highly heated solid-density material followed by the expansion of a liquid-density shell away from the sample surface.[17] The shell is filled with a two-phase mixture, composed of neutral and ionized silicons.[16] In this work it is proposed that the expansion of the delaminated film from the substrate is driven by a combination of two forces: the relaxation of intrinsic stress in the film,[12] and the interaction of the electron plasma and expanding ablated substrate material with the delaminated film associated with the femtosecond laser induced breakdown of the material.

The observation of the telephone cord instability (Fig. 5) is an indication of biaxial compressive stress,[14] suggesting that the compressive stress plays a role in blister formation under the experimental conditions used in this study, in contrast to experiments performed by other groups.[12] Given the time scale of blister formation presented above, additional laser material interaction may occur when the laser pulse has a duration that is a significant fraction of the initial blister growth time (around 1.6 ns for a 54 nm thermal oxide film at a laser fluence of 0.8 J/cm^2). The work presented here utilized laser pulses of duration (150 fs) much shorter than any expected physical change to the material,[17] which may not have been the case in Ref. 12 where laser pulses of 0.9 ns duration were used. The blister creation is then a response to an impulse, a feature attributed to the deterministic nature of femtosecond laser material interaction.[18]

We suggest that the thermal oxide film is heated and subsequently softened due to its proximity to the molten substrate[12] and by the dense electron plasma formed upon initial absorption of laser energy by the Si (100) substrate. Although not affected directly by the incident laser pulse, the thermal oxide film is likely heated to temperatures sufficient for softening due to its proximity to the substrate where material is melted by the incident laser pulse. Prior to this conductive heating, energetic electrons from the dense plasma may scatter into the thermal oxide film where they, in turn, shed energy through collisions, resulting in a heating of the film. Once the film is delaminated from the substrate, momentum is transferred from the expanding ablated substrate material[15] to the softened film resulting in blister features of dimensions exceeding those predicted by compressive stress relaxation alone. Preliminary calculations of the fracture energy and fracture toughness were performed using the dimensions of the blisters and the mechanical and physical properties of the film and substrate.[19,20] The results of this initial analysis yielded fracture energy and toughness values two to three times lower than those of bulk silicon and SiO$_2$, providing further support that another mechanism, in addition to compressive stress relaxation, is participating in the creation of the blister features. A complete analysis of the mechanical properties of the blisters is focus of future work.

In summary, we have observed blister or bubble formation in thermally grown oxide films on Si (100) after irradiation with single and multiple femtosecond laser pulses. The shape and dimensions of the blisters vary with the film thickness and incident laser energy. The mechanism responsible for the formation of the blister is thought to be a combination of compressive stress relaxation and the forced expansion of the softened film by material ablated from the substrate. Potential applications of this blister formation technique include capillaries and channels for micro- and nanofluidics.

This work was funded by the NSF (Grant No. DMR03070400) and the DARPA/AFOSR (Grant No. FA9550-04-0136).

[1] J. Bonse, S. Baudach, J. Kruger, W. Kautek, and M. Lenzner, Appl. Phys. A: Mater. Sci. Process. **74**, 19 (2002).
[2] H. O. Jeschke, M. E. Garcia, M. Lenzner, J. Bonse, J. Kruger, and W. Kautek, Appl. Surf. Sci. **197-198**, 839 (2002).
[3] B. K. A. Ngoi, K. Venkatakrishnan, E. N. L. Lim, B. Tan, and L. H. K. Koh, Opt. Lasers Eng. **35**, 361 (2001).
[4] J. Bonse, K. W. Brzezinka, and A. J. Meixner, Appl. Surf. Sci. **221**, 215 (2004).
[5] A. P. Singh, A. Kapoor, K. N. Tripathi, and G. R. Kumar, Opt. Laser Technol. **34**, 37 (2002).
[6] K. Sokolowski-Tinten, J. Bialkowski, A. Cavalleri, D. von der Linde, A. Oparin, J. Meyer-ter-Vehn, and S. I. Anisimov, Phys. Rev. Lett. **81**, 224 (1998).
[7] A. J. Pedraza, S. Jesse, Y. F. Guan, and J. D. Fowlkes, J. Mater. Res. **16**, 3599 (2001).
[8] A. P. Joglekar, H. Liu, G. J. Spooner, E. Meyhofer, G. Mourou, and A. J. Hunt, Appl. Phys. B: Lasers Opt. **77**, 25 (2003).
[9] T. Q. Jia, Z. Z. Xu, R. X. Li, D. H. Feng, X. X. Li, C. F. Cheng, H. Y. Sun, N. S. Xu, and H. Z. Wang, J. Appl. Phys. **95**, 5166 (2004).
[10] C. B. Schaffer, A. Brodeur, and E. Mazur, Meas. Sci. Technol. **12**, 1784 (2001).
[11] J. R. Serrano and D. G. Cahill, J. Appl. Phys. **92**, 7606 (2002).
[12] J. R. Serrano and D. G. Cahill, Microscale Thermophys. Eng. **9**, 155 (2005).
[13] K. Xiao, Z. S. Guan, G. J. Wang, L. Jiang, D. B. Zhu, and Y. R. Wang, Appl. Phys. Lett. **85**, 1934 (2004).
[14] H. Y. Yu, C. Kim, and S. C. Sanday, Thin Solid Films **196**, 229 (1991).
[15] D. von der Linde and K. Sokolowskit-Tinten, Appl. Surf. Sci. **154**, 1 (2000).
[16] B. Rethfeld, K. Sokolowski-Tinten, D. Von der Linde, and S. I. Anisimov, Appl. Phys. A: Mater. Sci. Process. **79**, 767 (2004).
[17] K. Sokolowski-Tinten, J. Bialkowski, A. Cavalleri, D. von der Linde, A. Oparin, J. Meyer-ter-Vehn, and S. I. Anisimov, Phys. Rev. Lett. **81**, 224 (1998).
[18] A. P. Joglekar, H. Liu, G. J. Spooner, E. Meyhofer, G. Mourou, and A. J. Hunt, Appl. Phys. B: Lasers Opt. **77**, 25 (2003).
[19] J. W. Hutchinson and Z. Suo, Adv. Appl. Mech. **29**, 63 (1992).
[20] D. B. Marshall and A. G. Evans, J. Appl. Phys. **56**, 2632 (1984).