Molecular Dynamics Simulations of Ion-Induced Rearrangement of Ultrathin Oxide Films on Silicon

Alison A. Kubota and Demeter J. Economou

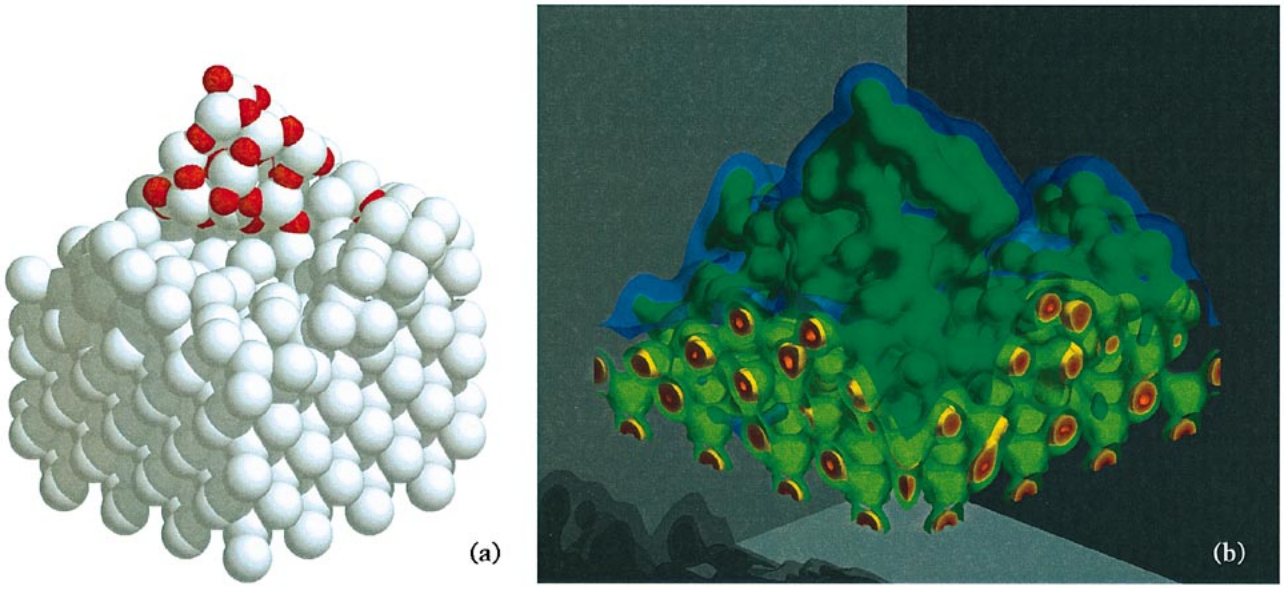

Fig. 1. (a) An off-axis view of a space filling representation of an oxide island formed after successive 100 eV argon ion bombardment at normal incidence and a fluence of 38 monolayers (1216 ions). The white and red spheres represent Si and O atoms, respectively. The sphere radii have been chosen arbitrarily to provide optimal viewing of the surface. (b) Constant energy surfaces for the cell shown at left. The outer transparent blue surface corresponds to a potential of approximately 2 eV. Higher energies are probed in green (50 eV) and yellow-orange (>100 eV).

***Abstract*— We present three-dimensional images of ion-irradiated ultrathin oxide films on silicon surfaces, generated from molecular dynamics simulations. The surface has the tendency to form oxide islands as the film is sputtered away by 100 eV Ar^+ ions. We also show an image of a "peeling" oxide strand which forms occasionally as a result of ions impacting at an angle of 45° from normal.**

***Index Terms*—Oxide islands, sputtering, surface cleaning.**

WE have simulated low energy argon ion beam irradiation and sputtering of ultrathin oxide layers on silicon surfaces using the technique of molecular dynamics (MD). Ultrathin oxide films of approximately 2.3 monolayers (ML) on Si(100) initially (2×1)-reconstructed surfaces were formed by chemisorption of O atoms. O-atom chemisorption followed Langmuir kinetics with an initial sticking probability of O on silicon equal to unity. The MD cell was 11–16 Å high and had an exposed area of 472 $Å^2$. Case studies involved normally incident and off-normal (45° and 75°) 100 eV Ar^+ ions impacting the oxidized silicon surface. The lattice temperature was varied from 300–973 K to examine the dependence of oxide removal rate (cleaning) on substrate temperature and incident ion angle to complement the experimental results of Lee *et al.* [1]. Lattices shown in this report were kept at 300 K, and ion doses of up to ~100 ML (3200 ions) were typically used. A reparameterized Jiang and Brown [2], [3] potential was used, while Ar interactions with Si and O were modeled using the Moliere potential. Details and further results of the simulations are published elsewhere [4].

When subjected to successive ion irradiation, the oxide film was found to undergo structural and compositional changes with increasing Ar^+ fluence. For example, the O-to-Si sputtering yield ratio varied with increasing ion fluence. In the limit of reduced oxygen content of the surface, the sputter yield for normally incident 100 eV Ar^+ was found to be approximately 0.03, comparable to the sputtering yield of pure silicon [5], [6].

In the regime of 0.5–1.5 ML oxygen content, the surface appeared to take on island-like formations ~2–5 Å thick. Such oxide islands have also been observed in experimental studies of the oxidation of silicon [7]. It has been shown that 750 eV ion irradiation enhances the rate of silicon oxidation due

Manuscript received July 7, 1998. This work was supported by the National Science Foundation (CTS-9713262) and the State of Texas through the Texas Advanced Technology Program.

The authors are with the Plasma Processing Laboratory, Department of Chemical Engineering, University of Houston, Houston, TX 77204-4792 USA (e-mail: economou@uh.edu).

Publisher Item Identifier S 0093-3813(99)02414-5.

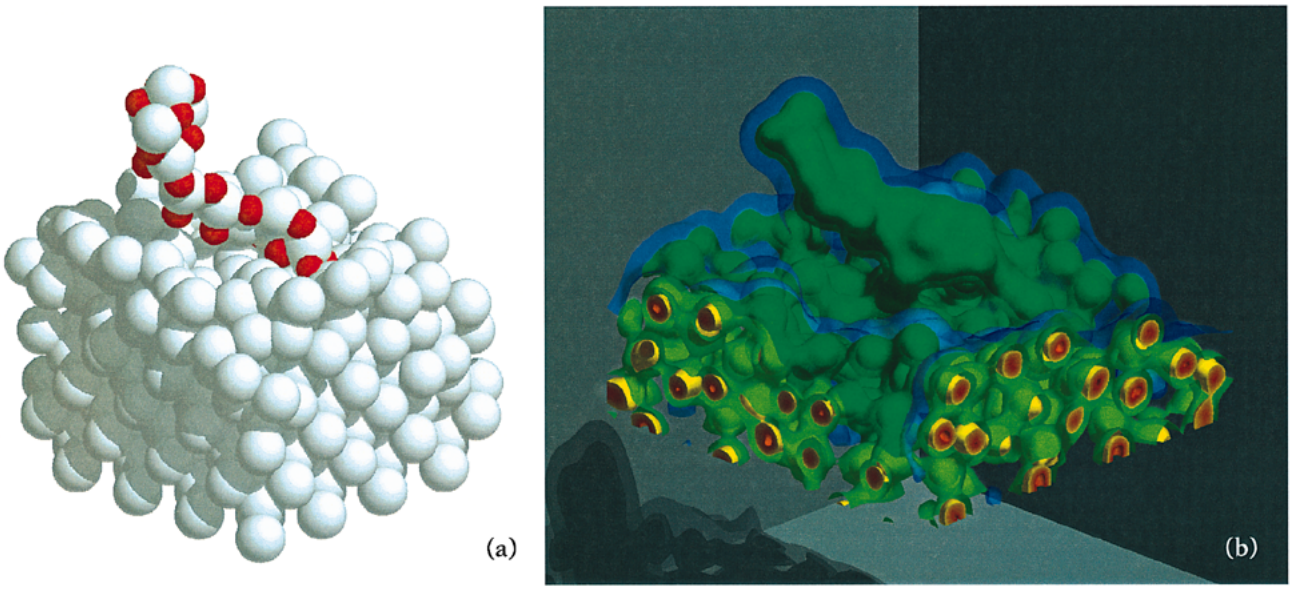

Fig. 2. (a) An off-axis view of a space filling representation of a "peeled" oxide strand formed after successive 100 eV argon ion bombardment at 45 ° off normal incidence and a fluence of 30 monolayers (960 ions). (b) Constant energy surfaces for the cell shown at left. Other details as in Fig. 1.

to enhanced oxygen transport and diffusion in the oxide layer [8]. An ion-enhanced diffusion mechanism may be responsible for the formation of the islands observed in our study.

Fig. 1 shows an off-axis rendering graphic of an oxidized silicon surface after exposure to 38 ML (1216 ions) of 100 eV normally incident Ar^+. Although the oxygen distribution was rather uniform on the original surface, an oxide island forms on the ion-irradiated surface, which also increases the surface roughness. The rms roughness was calculated to be approximately 4 Å, higher than the initial oxidized silicon surface roughness of 1.5 Å. Although only one island is shown in Fig. 1, two and, rarely, three islands could statistically form on the surface as a function of ion fluence. The island size could be affected by the limited computational cell size but this effect was not studied. On rare occasions, short lived metastable configurations as shown in Fig. 2 were observed. The lattice of Fig. 2 was computed after an ion dose of 30 ML (960 ions) of 100 eV Ar^+ impacting at 45° from normal. The effect of off-normal ion impact was to increase the film removal rate, as well as generate configurations such as shown in Fig. 2. Initially an oxide "strand" on the surface, this configuration formed after further ion impact which caused "shaking" and "peeling" of the island over the short time scales simulated using MD. The projected size of the strand is substantially smaller than the cell size. Therefore the strand does not appear to be an artifact of the periodic boundary conditions. The simulation was not run long enough in between ion impacts to check the stability of the strands against desorption. However, there were cases where a peeled strand could be sputtered away by an incident ion. Figs. 1(b) and 2(b) show surfaces of constant potential of the respective lattices. The outer transparent blue surface corresponds to a potential of approximately 2 eV. Higher energies are probed in green (50 eV) and yellow-orange ($>$100 eV) surfaces. These higher energies can be thought as scattering barriers seen by high energy ions that can penetrate into the lattice.

Figs. 1(a) and 2(a) were rendered using Rasmol [9] molecular visualization software. Further techniques have been developed to provide rapid generation of time-resolved animation of simulation results.

ACKNOWLEDGMENT

The authors would like to thank D. C. McCleney for her greatly informative discussions and assistance in performing the visualization tasks, specifically Figs. 1(b) and 2(b).

REFERENCES

[1] S. M. Lee, C. J. Fell, D. Marton, and J. W. Rabalais, "Synergistic effects in annealing and low energy ion bombardment of Si(100) surfaces," *J. Appl. Phys.*, vol. 83, pp. 5217–5223, 1998.

[2] Z. Jiang and R. A. Brown, "Modeling oxygen defects in silicon crystals using an empirical interatomic potential," *Chem. Eng. Sci.*, vol. 49, pp. 2991–3000, 1994.

[3] Z. Jiang and R. A. Brown, "Atomistic calculation of oxygen diffusivity in crystalline silicon," *Phys. Rev. Lett.*, vol. 74, pp. 2046–2049, 1995.

[4] N. A. Kubota, "Molecular dynamics simulations of plasma surface interactions for microelectronics processing applications," Ph.D. dissertation, Dep. Chem. Eng., Univ. Houston, Aug. 1998.

[5] P. C. Zalm, "Energy dependence of the sputtering yield of silicon bombarded with neon, argon, krypton, and xenon ions," *J. Appl. Phys.*, vol. 54, pp. 2660–2666, 1983.

[6] N. A. Kubota and D. J. Economou, "Molecular dynamics simulations of low-energy (25–200 eV) argon ion interactions with silicon surfaces: Sputter yields and product formation pathways," *J. Appl. Phys.*, vol. 83, pp. 4055–4063, 1998.

[7] T. Horie, Y. Takakuwa, and N. Miyamoto, "Two-dimensional growth and decomposition of initial thermal SiO_2 layer on Si(100)," *Jpn. J. Appl. Phys.*, vol. 33, pp. 4684–4690, 1994.

[8] J. R. Engstrom, D.J. Bonser, and T. Engel, "The reaction of atomic oxygen with Si(100) and Si(111). II. Adsorption, passive oxidation and the effect of coincident ion bombardment," *Surf. Sci.*, vol. 268, pp. 238–264, 1992.

[9] *RasMol Molecular Graphics Visualization Tool*, R. A. Sayle, Glaxo Research and Development, Biomolecular Structures Group, 1994.