

Effect of Ba on the oxidation of the Si(100) surface

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(Received 15 October 1990; revised manuscript received 30 January 1991)

Si oxidation in the Ba/Si(110) system has been studied by Auger-electron spectroscopy (AES) and low-energy electron diffraction as a function of Ba and oxygen exposure. The rate of the Si oxidation under elevated temperatures has been shown to be significantly enhanced by monolayer (ML) amounts of Ba. Under very high Ba exposures (≈ 4 ML), the Si oxidation in the Ba/Si(100) system was, however, promoted more rapidly at room temperature than at 700°C. AES data have also shown the formation of Ba silicide after Ba exposures of > 1 ML and anneal to about 600°C.

I. INTRODUCTION

The effect of metal overlayers on the oxidation of a Si surface has been an interesting subject for a number of years,¹⁻¹¹ due to the importance of low-temperature Si oxidation in the fabrication of microelectronics devices.¹² For example, it is already well known that the adsorption of an alkali-metal element on a silicon surface can result in a dramatic enhancement of surface reactivity to oxygen.¹⁻⁵ The mechanism for metal-promoted Si oxidation has already been proposed.^{1,4,6} It is believed that the change of surface chemical activity was a result of charge transfer between substrate and metal overlayer.

Meanwhile, since the recent discovery of high-temperature superconductors (HTSC's), such as the Y-Ba-Cu-O (Refs. 13-16) and Sr-Bi-Cu-O (Ref. 17) compounds, the interaction of the HTSC constituent elements with substrate materials has resulted in problems in stabilizing the HTSC film on the surfaces, thus hampering the prospect of integrating HTSC with other materials especially semiconductors such as Si.¹⁸ Therefore the investigation of the interaction of the HTSC constituent elements with various substrates has become more interesting. As a result, the surface systems of Bi/Si(100) (Ref. 19) and Sr/Si(100) (Refs. 20 and 21) were investigated to understand their interfacial structures and the effect of the metal elements on the surface chemical properties of silicon.

In this paper we report the studies of the interaction of Ba with the Si(100) surface and the reaction of the Ba/Si(100) system to oxygen exposure at different substrate temperatures.

II. EXPERIMENT

The experiments were carried out in an ultra high-vacuum (UHV) chamber equipped with a four-grid low-energy electron diffraction (LEED) optics which was also used as a retarding field analyzer for Auger-electron spectroscopy (AES). The experimental conditions were essentially the same as those for the previous work.^{19,20} The Si(100) samples was a piece of *p*-type Si wafer with resistivity of 80 Ω cm, lightly doped with boron which was not expected to affect the Si oxidation study. The Si(100)

surface was cleaned in UHV by Ar⁺ ion bombardment and annealed to 1100°C and 700°C, resulting in a clear (1×2) LEED pattern of the expected surface reconstruction.

The Ba source was a small piece of bulk Ba in a cell made of thin Ta foil and heated electrically. The deposition rate of Ba was calibrated by a quartz-crystal microbalance. The Ba exposure was measured in units of monolayer [1 ML = 6.8×10^{14} atoms/cm², equal to the atomic density of the Si(100) surface], and the oxygen exposure was in units of langmuir (1 L $\equiv 1 \times 10^{-6}$ Torr sec). The base pressure of the UHV chamber during the course of the experiments was below 2×10^{-10} Torr.

III. RESULTS AND DISCUSSIONS

Oxidation of silicon in the Ba/Si(100) system has been measured at both room temperature and 700°C as a function of barium and oxygen exposures. Desorption of Si oxides such as SiO should not be significant at 700°C (Ref. 5) and was undetected in our experiments, though it has been previously detected at small submonolayer oxygen coverage (< 1 ML).²² The oxidation process, however, is expected to be more dramatic at the elevated temperature, thus the Si oxidation of the Ba/Si(100) system was first studied at 700°C.

For verification of the characteristic changes in the Auger spectra in response to the Si oxidation, the Auger electron spectra for both the Ba/Si(100) and the clean Si(100) surfaces were measured before and after exposed to oxygen at 700°C. Before O₂ exposure, as shown in Figs. 1(a) and 1(b), the deposition of Ba onto the clean Si(100) surface generated major Auger peaks at about 52 and 74 eV, and resulted in only a minor change in the shape of the Si AES peak at 92 eV. The Ba Auger peak at 52 eV is most distinctive and sensitive to the increasing Ba exposure, and was chosen for measuring the Ba surface concentration of the Ba/Si(100) system. After oxygen exposure, additional peaks were produced at 63 and 76 eV, as seen in Figs. 1(c) and 1(d). Among the peaks resulting from oxidation, the peak at about 63 eV is not overlapping with any major peak, and distinctive enough to represent the Si surface oxidation.

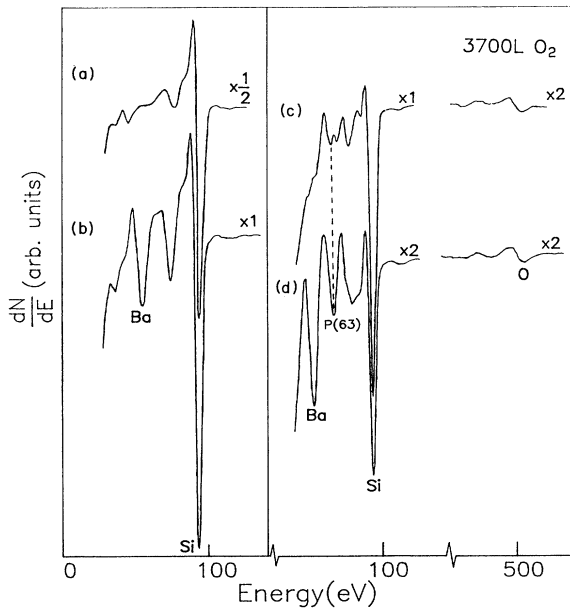


FIG. 1. Auger-electron spectra for (a) clean Si(100) surface and (b) Ba/Si(100) system after ~ 0.7 ML Ba exposure; (c) Si(100) surface exposed to 3700 L O₂ at 700°C and (d) Ba/Si(100) surface with ~ 0.7 ML Ba exposed to 3700 L O₂ at 700°C.

By measuring Si oxidation from the height of the Auger peak at 63 eV, it is clear from Fig. 1 that the Ba/Si(100) surface was much more reactive to oxygen than the clean Si surface. The Auger peak-to-peak ratio $I(\text{Si}(63 \text{ eV}))/I(\text{Si}(92 \text{ eV}))$ of the oxidized silicon to the nonoxidized silicon for the Ba/Si(100) surface is as much as four times that for the Si(100) surface, indicating a strong promotion of Si oxidation by Ba. The Auger spectra from the oxidized surface in Fig. 1 showed no obvious changes during further annealing at 700°C in vacuum (2×10^{-10} Torr). This confirmed that the SiO desorption at 700°C was insignificant.

The Ba-promoted Si oxidation was further investigated at 700°C as a function of Ba and O₂ exposures. Figure 2 shows the Si Auger peak ratio $I(\text{Si}(63 \text{ eV}))/I(\text{Si}(92 \text{ eV}))$, as a function of oxygen exposure, for the oxidation of the Ba/Si(100) system under different Ba exposures. Each data point in Fig. 2 was obtained by first exposing the room-temperature Si(100) to a specific Ba flux, and then exposing to oxygen after slowly heating to 700°C. Before the next Ba exposure, the deposited Ba and the oxidized Si on the surface were thoroughly cleaned off by Ar⁺ ion (1.5 keV) bombardments and anneals to 1100°C and 700°C.

As a general behavior for the Ba/Si(100) system, the Si Auger ratio $I(\text{Si}(63 \text{ eV}))/I(\text{Si}(92 \text{ eV}))$ initially increased dramatically with increasing O₂ exposure. At high oxygen exposure ($> 10^3$ L), however, the behavior of the Si oxidation was different under different Ba exposure. For the Ba exposures under 1 ML, further increase of oxygen exposure resulted in only a marginal increase of the Si

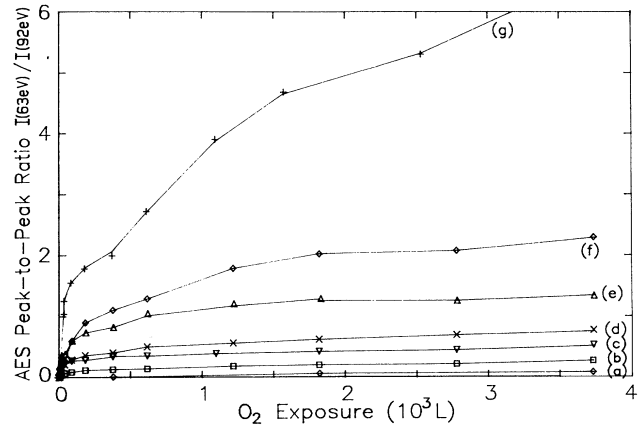


FIG. 2. Si Auger peak-to-peak ratio $[I(\text{Si}(63 \text{ eV}))/I(\text{Si}(92 \text{ eV}))]$ as a function of oxygen exposure for the 700°C Ba/Si(100) system under Ba exposures of (a) 0 ML, (b) 0.4 ML, (c) 0.7 ML, (d) 1 ML, (e) 1.5 ML, (f) 2.5 ML, and (g) 4.5 ML.

Auger ratio. For high Ba exposures (> 1 ML), the Auger ratio started to measurably increase above $t \times 10^2$ L O₂ exposure and at high Ba exposure the Auger ratio increased significantly above 5×10^2 L, as seen in Figs. 2(e)–2(g).

It was very intriguing to observe the difference in the Si oxidation for various Ba exposures as shown in Fig. 2. For further understanding of the oxidation process for the Ba/Si(100) system, Auger-electron spectra of the Ba/Si(100) system were examined as a function of temperature and oxygen exposure. Figure 3 shows Auger electron spectra for the Ba/Si(100) system under two different Ba exposures, 1 and 4 ML, respectively. After deposition of 1 ML Ba onto the room-temperature Si(100) surface, AES spectra were measured at both room temperature and 700°C, however, showing the same line shape as seen in Fig. 3(a). For this case of 1 ML Ba exposure, the oxidation process was essentially the same as that for Fig. 1(d), but the surface was more reactive. The Auger ratio $I(\text{Si}(63 \text{ eV}))/I(\text{Si}(92 \text{ eV}))$ for the Si oxidation in Fig. 3(d) after 390 L O₂ exposure is larger than that in Fig. 1(d) after 3700 L O₂ exposure.

However, after 4 ML Ba deposition onto the surface at room temperature, the AES spectrum [Fig. 3(e)] showed significant changes as the surface was slowly heated to 700°C [Fig. 3(f)]. The Ba(52 eV) Auger peak decreased and the Si(92 eV) Auger peak increased, as shown in Fig. 3(f), indicating a decrease of the Ba surface concentration due to Ba desorption. In addition to the decrease of the Ba concentration [measured here by the decrease in the Auger ratio of $I(\text{Ba}(52 \text{ eV}))/I(\text{Si}(92 \text{ eV}))$], a new Auger peak at about 85 eV was generated under annealing to 700°C [Fig. 3(f)]. This new Auger peak, not observed under lower Ba exposures (< 1.5 ML), clearly indicated the formation of a barium silicide. Therefore the decrease of the Ba surface concentration was also associated with Ba diffusion to form Ba silicide, additional to the desorption of Ba atoms from the surface.

When the Ba/Si(100) system was exposed to oxygen at 700°C, the 85-eV Auger peak of the Ba silicide disappeared with increasing oxygen exposure. In addition, the oxidized Si peak at 63 eV increased, and the Si(92 eV) Auger peak decreased drastically though the Ba(52 eV) peak remained almost unchanged. The disappearance of the barium silicide Auger peak indicates a dissociation of the silicide under oxidation, similar to that observed for other metal silicides such as Ce silicide.⁷

It is already clear from Fig. 2, that the Ba-promoted Si surface oxidation is proportional to the Ba deposited on the surface, since the Auger ratio increases with increasing Ba exposure. However, for a more complete picture of the Ba-promoted Si oxidation, the Auger ratio for the Si oxidation at 700°C has been depicted in Fig. 4 as a function of Ba exposure. The Si oxidation of the Ba/Si(100) system increased more drastically with Ba deposition up to ≈ 3 ML. However, after more than 5 ML Ba was deposited to the Si(100), as shown in Fig. 4, a slow down or a tendency to saturation of the Ba-promoted Si oxidation was reached. The slow down in the oxidation could be related to the Ba silicide formation generating a unique surface chemical configuration.

For a further confirmation of the Ba silicide formation in the Ba/Si(100) system, the Ba surface concentration was measured at both room temperature and 700°C as a

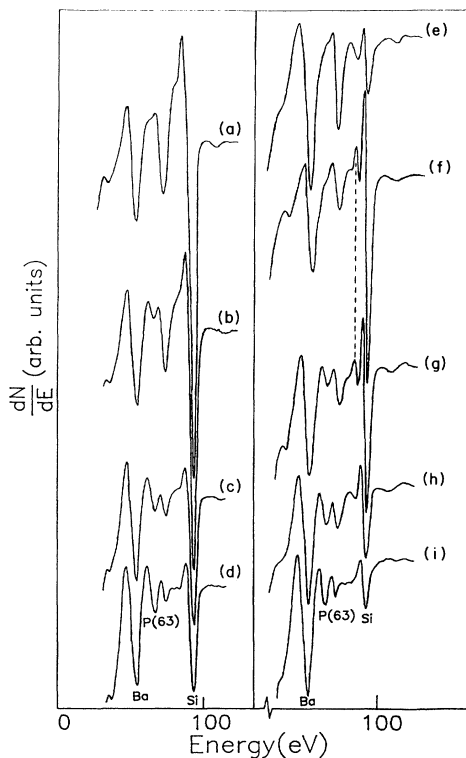


FIG. 3. Auger-electron spectra for the Ba/Si(100) system (left panel), with 1 ML Ba exposure (a) at room temperature, and after exposure to (b) 18 L, (c) 90 L, (d) 390 L oxygen at 700°C; (right panel) with ~ 4 ML Ba exposure (e) at room temperature and (f) at 700°C, and after exposure to (g) 6 L, (h) 18 L, (i) 42 L oxygen at 700°C.

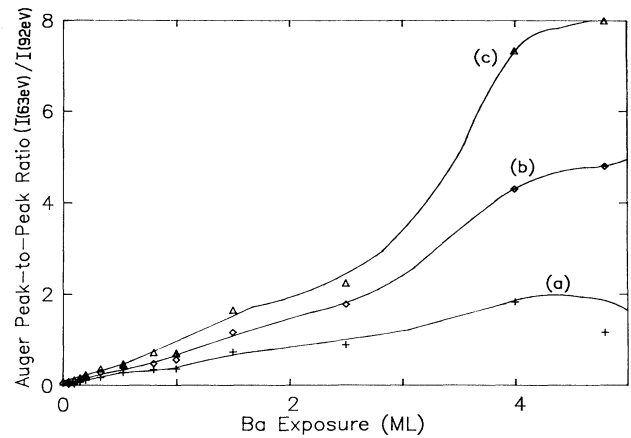


FIG. 4. Si Auger peak-to-peak ratio $[I(\text{Si}(63 \text{ eV}))/I(\text{Si}(92 \text{ eV}))]$ as a function of Ba deposition for the Ba/Si(100) system at about 700°C after exposure of (a) 180 L, (b) 1200 L, and (c) 3700 L oxygen.

function of Ba exposure [Figs. 5(a) and 5(b)]. As shown in Fig. 5(b), Ba deposition onto the room-temperature Si(100) surface resulted in continuous increase of the Ba surface concentration as Ba exposure increased. However, after annealing to 700°C, the Ba concentration decreased drastically and remained almost constant at Ba exposures greater than 2 ML [Fig. 5(a)]. Compared with the oxidation data in Figs. 2 and 4, it is obvious that the decrease in Ba concentration was due to not only Ba desorption from the surface but also Ba diffusion and formation of Ba silicide. As a result of the Ba diffusion, the Si oxidation in the Ba/Si(100) still increased after the Ba surface concentration reached a constant value. Therefore the increase of Si oxidation in the Ba/Si(100) (> 1 ML Ba exposure), seen in Figs. 2 and 4, was due to the Si

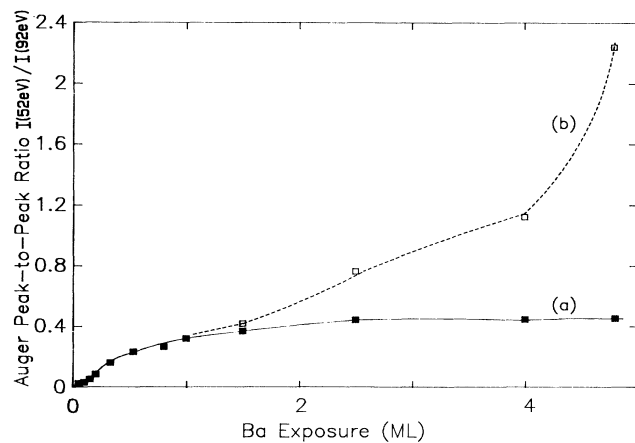


FIG. 5. Auger peak-to-peak ratio of $I(\text{Ba}(52 \text{ eV}))/I(\text{Si}(92 \text{ eV}))$ for the Ba/Si(100) system (a) just after Ba deposition at room temperature and (b) after annealing to about 700°C. Solid and dashed curves are to aid the eye.

oxidation in the Ba silicide since metal silicides are usually more reactive to oxygen than clean Si surfaces.^{6,11} It should be noted here that under low Ba exposures (< 1 ML), the Ba atoms in the Ba/Si(100) system formed a number of ordered surface atomic structures at high temperatures less than 1000 °C, rather than desorbing from or diffusing into the surface.²²

The significant difference in the Ba concentration [Figs. 5(a) and 5(b)], due to different substrate temperatures, could also impact the Ba promotion of Si oxidation. Therefore the Si oxidation study in the Ba/Si(100) system was also done at room temperature as a function of both Ba and oxygen exposures.

Figure 6 shows the Si Auger ratio $I(\text{Si}(63 \text{ eV}))/I(\text{Si}(92 \text{ eV}))$ for Si oxidation in the room-temperature Ba/Si(100) system as a function of Ba exposure. From the data in Fig. 6, it is clear that Si oxidation in the Ba/Si(100) increased dramatically at room temperature even at Ba exposures above 4 ML. Compared with the Auger data in Fig. 4 for 700 °C, the behavior of the Auger ratio in Fig. 6 did not indicate any saturation of the Ba promoted Si oxidation. Furthermore, compared with the data in Fig. 4 after 3700 L O₂ exposure, the Si oxidation in the Ba/Si(100) at room temperature and high Ba exposure (> 4 ML) was surprisingly more significant than at 700 °C.

The promotion of the room-temperature Si oxidation by multiatomic Ba layers was possibly due to a mechanism which may enhance the dissociation of oxygen molecules and thus enhance the reactivity of Si to oxygen. This room-temperature oxidation of Si, promoted by Ba, may have similarity to the Si oxidation promoted by multiatomic layers of alkali metals,^{1,4} though the chemical composition of the Si oxide layer may be quite different.

On the other hand, in response to the oxygen exposure, the behavior of Si oxidation at room temperature was also quite different from that at 700 °C. As shown in Fig. 7, the Si Auger ratio $I(\text{Si}(63 \text{ eV}))/I(\text{Si}(92 \text{ eV}))$ of the Si oxidation increased extremely rapidly when the surface

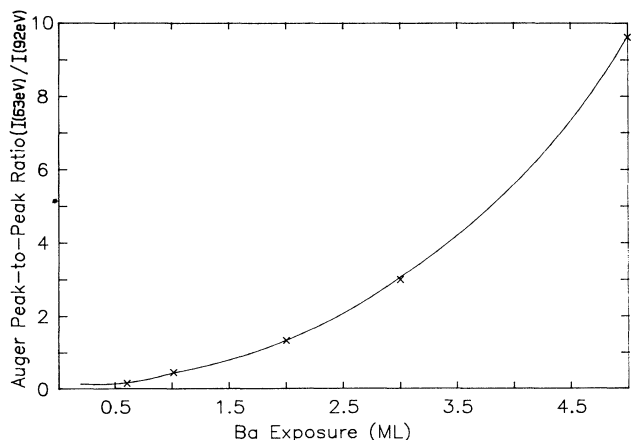


FIG. 6. Si Auger peak-to-peak ratio $[I(\text{Si}(63 \text{ eV}))/I(\text{Si}(92 \text{ eV}))]$ as a function of barium exposure for the room-temperature Ba/Si(100) system after exposure to 1440 L oxygen.

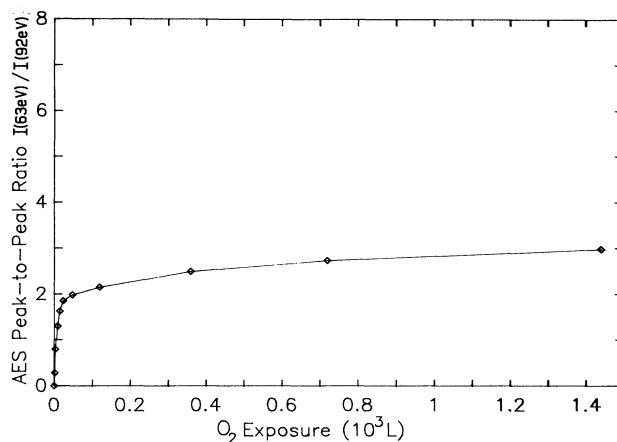


FIG. 7. Si Auger peak-to-peak ratio $[I(\text{Si}(63 \text{ eV}))/I(\text{Si}(92 \text{ eV}))]$ for oxidation at room temperature of the Ba/Si(100) system with 2 ML Ba as a function of oxygen exposure.

was exposed to the first 100 L oxygen. This behavior of the Si Auger ratio as a function of oxygen exposure was generally the same for the room-temperature Ba/Si(100) under different Ba exposures. The increase of the Auger ratio then became very slow after 500 L oxygen exposure, very different from the behavior observed at 700 °C for the Ba-silicide shown in Fig. 2. The significant increase of the Auger ratio after 500 L oxygen exposure, for the 700 °C samples as seen in Figs. 2(f) and 2(g), was not observed for the room-temperature Ba/Si(100) samples because the Ba atoms did not diffuse into the surface and form Ba silicide at room temperature.

The surface atomic structure of the oxidized Ba/Si(100) was examined frequently by LEED while exposed to oxygen. There were no new diffraction spots observed in the LEED pattern in response to the oxygen exposure. A general trend of the LEED pattern was drastic decrease of the LEED intensities, leading to final disappearance of the LEED pattern as oxygen exposure increased. Therefore the oxidized Si in the Ba/Si(100) system had no long-range ordered atomic structures.

The morphology of the oxidized surface of the Ba/Si(100) system could be more complicated than a layer structure, due to the diffusion of Ba atoms and formation of Ba silicide in the Ba/Si(100) system at 700 °C. Thus the simple models used for calculations^{19,21} may not be valid for the Ba/Si(100) system oxidized at 700 °C. However, the morphology of the Ba/Si(100) system oxidized at room temperature should be much simpler, and the simple model of an oxidized Si layer in the Ba/Si(100) system should be a good approximation.

By assuming that the Auger sensitivities of the peaks at 52 and 63 eV are still the same as for the bulk materials of Ba and SiO₂, one can calculate the thickness of the oxidized Si from the model, as described previously.²¹ The model calculation indicates that the thickness of the Si oxide is approximately 15 Å for the Ba/Si(100) system under ≈ 4 ML Ba exposure after exposure to 1440 L oxy-

gen at room temperature.

Finally, it should be pointed out here, that the formation of the Ba silicide might generate more difficulties in stabilizing a Ba-based HTSC film on the Si surface, due to the interdiffusion of the elements. However, low-temperature deposition ($T < 500^\circ\text{C}$) should be able to prevent the formation of the silicide and be beneficial to achieving a stable Ba-based HTSC film on Si surfaces. It is also possible to produce a thick layer of Ba silicide as a barrier to resist further diffusion of other elements.

IV. CONCLUSIONS

Si oxidation in the Ba/Si(100) system has been studied at both room temperature and 700°C as a function of Ba and oxygen exposures. At room temperature, Ba atoms deposited onto the Si surface did not form Ba silicide, however, they did drastically enhance the Si surface oxi-

dation. The promotion of Si oxidation in the Ba/Si(100) by Ba was directly proportional to the Ba exposure at room temperature. At 700°C , the Ba atoms partially diffused into the Si surface to form a barium silicide after 1 ML Ba exposure. The Ba-promoted Si oxidation in the Ba/Si(100) system was still proportional to Ba exposure (< 4 ML) at 700°C , though a trend toward saturation was detected at ~ 4 ML Ba exposure. Compared with the 700°C Si oxidation, the room-temperature oxidation of the Si surface was more drastic for the Ba/Si(100) system under high Ba exposure (> 2.5 ML).

ACKNOWLEDGMENTS

This work was supported in part by the R. A. Welch Foundation (Houston, TX), the Texas Center for Superconductivity at University of Houston (TCSUH), and NASA.

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- ¹J. E. Ortega, E. M. Oellig, J. Ferron, and R. Miranda, *Phys. Rev. B* **36**, 6213 (1987).
²A. Franciosi, P. Soukiassian, P. Philip, S. Chang, A. Wall, A. Raisanen, and N. Troullier, *Phys. Rev. B* **35**, 910 (1987).
³H. I. Starnberg, P. Soukiassian, M. H. Bakshi, and Z. Hurych, *Phys. Rev. B* **37**, 1315 (1988).
⁴E. G. Michel, E. M. Oellig, M. C. Asensio, and R. Miranda, *Surf. Sci.* **189/190**, 245 (1987).
⁵C. A. Papageorgopoulos, S. Foulas, S. Kennou, and M. Kamaratos, *Surf. Sci.* **211**, 991 (1989).
⁶P. Lomellini and S. Valeri, in *Dynamical Phenomena at Surfaces: Interfaces and Superlattices*, Vol. 3 of *Springer Series in Surface*, edited by F. Nizzoli, K. H. Rieder, and R. F. Willis (Springer-Verlag, New York, 1985), p. 244.
⁷F. U. Hillebrecht, M. Ronay, D. Rieger, and F. J. Himpsel, *Phys. Rev. B* **34**, 5377 (1986).
⁸P. Wetzl, C. Pirri, J. C. Peruchetti, D. Bolmont, and G. Gewinner, *Surf. Sci.* **178**, 27 (1986).
⁹P. J. Møller and J.-W. He, *J. Vac. Sci. Technol. A* **5**, 996 (1987).
¹⁰S. Chang, P. Philip, A. Wall, A. Raisanen, N. Troullier, and A. Franciosi, *Phys. Rev. B* **35**, 3013 (1987).
¹¹G. R. Castro, J. E. Hulse, and J. Koppers, *Appl. Surf. Sci.* **27**, 262 (1986).
¹²J. R. Brews, W. Fichner, E. H. Nicollian, and S. M. Size, *IEEE Electron Device Lett.* **EDL-1**, 2 (1980).
¹³J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986).
¹⁴C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, *Phys. Rev. Lett.* **58**, 495 (1987).
¹⁵J. R. Cava, R. B. van Dover, B. Batlogg, and E. A. Reitman, *Phys. Rev. Lett.* **58**, 408 (1987).
¹⁶M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang and C. W. Chu, *Phys. Rev. Lett.* **58**, 908 (1987).
¹⁷H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, *Jpn. J. Appl. Phys. Lett.* **27**, L209 (1988).
¹⁸C. T. Cheung and E. Rukenstein, *J. Mater. Res.* **4**, 1 (1989).
¹⁹W. C. Fan, A. Ignatiev, and N. J. Wu, *Surf. Sci.* **235**, 169 (1990).
²⁰W. C. Fan, N. J. Wu, and A. Ignatiev, *Phys. Rev. B* **42**, 1254 (1990).
²¹W. C. Fan, A. Mesarwi, and A. Ignatiev, *J. Vac. Sci. Technol. A* **8**, 4017 (1990).
²²W. C. Fan and A. Ignatiev, *Surf. Sci.* (to be published).