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The effect of steps on the oxidation of a caesiated Si(100)2 × 1 surface

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Abstract. Exposure of a caesiated Si(100)2 × 1 surface to O₂ and subsequent heating to about 800 °C caused the formation of SiO₄ and SiO₂. For a saturation Cs coverage and the same O₂ exposure, the growth of oxides is more pronounced on a stepped than on a non-stepped Si(100)2 × 1 surface. This is due to the higher coverage of Cs on the stepped surface. When the above oxidation cycle is repeated, the SiO₂ predominates. After six oxidation cycles the average thickness of SiO₂ is about 11 Å and 16 Å on Si(100)2 × 1 surfaces without and with steps, respectively.

1. Introduction

The Si–SiO₂ interfaces are very important in microelectronics. This is shown by the recent great interest in the oxidation of Si surfaces [1–5]. The direct oxidation of Si requires a relatively high temperature and pressure, which cause imperfections in the interface region [4].

In the last decade, there have been systematic studies on the co-adsorption of alkali and O₂ on metals and semiconductors which suggest that, regardless of the substrate, the presence of Cs increases drastically the sticking coefficient and the maximum amount of O₂ that can be deposited on the surface [6–8]. The presence of Cs also enhances the oxidation of some metal substrates [9]. These results suggest that Cs can be used as an additive to enhance the oxidation of Si. In fact, recent studies on the oxidation of Si surfaces suggest that the presence of Cs reduces the oxidation temperature and promotes the growth of the oxide [5, 10–12]. However, some problems exist. The thickness of the oxide is relatively small and it is not quite uniform [13]. Thus it is reasonable to look for an additional source of enhancement for the oxidation of Si surfaces besides the presence of alkali.

The steps on a Si surface might be helpful for further enhancement of the oxidation. The edge sites of the steps have more dangling bonds than do the sites on a regular Si plane [14]; this may increase the growth of Si oxide. In this work, a systematic experimental study of the oxidation of Si(100)2 × 1 surfaces with and without steps in the presence of Cs has been carried out.

2. Experimental details

Experiments were performed in a conventional UHV chamber equipped with a hemicylindrical mirror analyser for Auger electron spectroscopy (AES), four-grid optics for low-energy electron diffraction (LEED), a quadrupole mass spectrometer for thermal desorption (TDS) and facilities for work function (WF) measurements using the electron beam diode method. Cs was evaporated from a commercial SAES-Getters source and the background pressure during deposition was kept below 10^{-10} Torr. The Cs flux used in the experiments, as measured with a Pt ioniser, was 1.0×10^{12} atoms $\text{cm}^{-2} \text{s}^{-1}$ and could be kept stable within 5% even for the largest exposures. Spectroscopically pure O_2 was admitted to the system through a bakeable leak valve. The partial pressure of O_2 during exposure was 5×10^{-8} Torr. The O_2 pressure was monitored with a quadrupole mass spectrometer. During the AES measurements the beam current and modulation voltage were $2 \mu\text{A}$ and 4V , respectively, while the background pressure was below 10^{-10} Torr. Two Si crystals $10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$ in size were simultaneously mounted inside the chamber, one of them with its surface parallel to the (100) crystallographic plane within $\pm 0.2^\circ$ and the other one with its surface 5° off this plane in the [110] zone. Both crystals were n type with resistivities of $10^{-2} \Omega \text{ cm}$ (plane) and $100 \Omega \text{ cm}$ (vicinal), respectively. The samples could be heated by passing current through a Ta strip uniformly pressed between the crystal and a Ta foil case. The sample temperature was measured with a (Ni–Cr)/(Ni–Al) thermocouple spot welded on the case and calibrated with an IR pyrometer.

The crystals, which had also been used in a previous study [15], were initially cleaned with successive Ar^+ bombardment and annealing cycles at about 1100 K. On exposure to the atmosphere the main contaminant of both surfaces was C which could be eliminated by heating to about 1400 K. After cleaning, all contaminants were below the AES detection limit, the plane (100) surface exhibited the usual reconstructed (2×1) LEED pattern, while the LEED pattern of the vicinal surface showed the characteristic single-double spot succession with varying electron energy as expected from a regularly stepped surface. Analysis of the energy dependence of the integral spot splitting led to a step height of about $\alpha_0/2$, where $\alpha_0 = 5.43 \text{ \AA}$ is the Si unit-cell parameter, and an average terrace width of about 30 \AA . These values are in agreement with those found in the literature for similarly cleaned 5° vicinal Si(100) surfaces [16].

3. Results and discussion

3.1. Cs adsorption

The behaviour of Cs on Si(100) 2×1 with and without steps has been studied recently in our laboratory [17]. Briefly, the findings which are related to this paper are the following. Cs adsorbs initially on the edge sites of the steps and subsequently on the terraces. The presence of the steps increases the sticking coefficient and the maximum amount of Cs that can be deposited on Si(100) 2×1 . The increase in the sticking coefficient was about 50% and was estimated from the AES curves and the measured Cs flux. This implies that the sticking coefficient of Cs on flat Si(100) is less than unity.

3.2. O_2 adsorption

Figure 1(a) shows the WF change $\Delta\Phi$ against O_2 exposure on Si(100) 2×1 with and without steps. First, we should mention that the WF value of clean stepped Si(100) 2×1

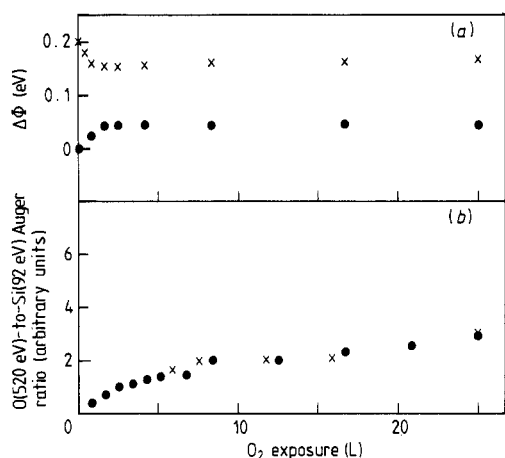


Figure 1. (a) WF change and (b) the O(520 eV)/Si(92 eV) Auger peak-to-peak height ratio against O₂ exposure on Si(100)2 × 1 with (●) and without (×) steps. (The Si(92 eV) peak height corresponds to the clean substrate before each measurement.)

was found to be 0.2 eV greater than that of the flat crystal. This is consistent with theoretical work which suggests that the WF of a Si(111) surface with steps is greater than that without steps [14] and agrees qualitatively with experimental data on p-type Si(111) [18]. Our experimental data in figure 1(a) show that deposition of O on the flat surface causes a small increase in the WF, while on the stepped surface the WF decreases. A possible explanation is that the centre of mass of the initially deposited O atoms near the steps lies below the top atom row of the stepped surface. Thus the resultant surface dipole moment has an outward direction which leads to the WF decrease. These small differences could also be attributed to changes in the surface band bending.

Figure 1(b) shows the O(520 eV)/Si(92 eV) Auger peak-to-peak height ratio plotted against O₂ exposure on Si(100)2 × 1 surfaces with and without steps. (The height of the Si(92 eV) peak is always that of the clean substrate before each measurement.) This figure indicates that both the adsorption rate and the maximum amount of O are about the same on the flat and stepped Si(100)2 × 1 surfaces.

3.3. Adsorption of O₂ on caesiated Si(100)2 × 1

3.3.1. AES measurements. Figures 2(a) and 2(b) show the ratio of O(520 eV)/Si(92 eV) Auger peak heights plotted against O₂ exposure on caesiated Si(100)2 × 1 surfaces without and with steps, respectively, after various Cs exposures. A comparison of these figures with figure 1(b) suggests that the increasing coverage of pre-deposited Cs increases drastically the sticking coefficient and the maximum amount of O on the surface, in agreement with existing studies on metals and semiconductors [7, 8]. Figure 2 also shows that the presence of steps causes a further increase in the amount of adsorbed O for the same O₂ exposure. According to [7], the adsorption of O on caesiated metal surfaces is controlled by the Cs overlayer. In the present case, the steps increase the Cs coverage which in turn causes further increase in the adsorbed O.

3.3.2. WF measurements. Figure 3 shows the WF changes upon O₂ adsorption on caesiated surfaces of Si(100)2 × 1 with steps. The broken curve shows the WF change on Cs deposition on a clean stepped Si(100)2 × 1 surface which has been discussed elsewhere [17]. The full circles show the WF change on O₂ exposure starting at various levels of Cs deposition. The exposure increases along the x axis and the length of the arrow

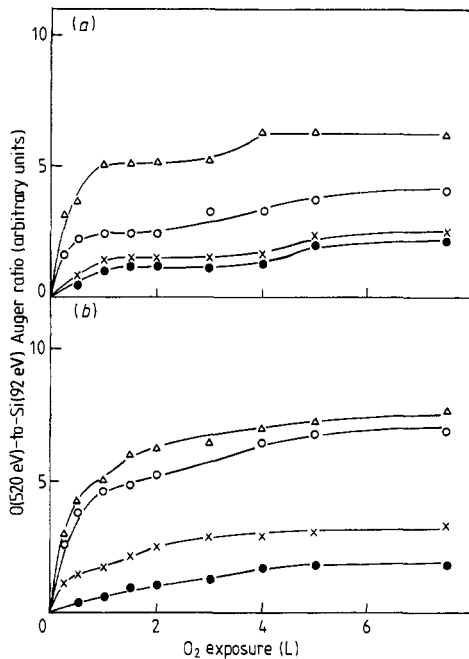


Figure 2. The O(520 eV)/Si(92 eV) Auger peak-to-peak height ratio against O₂ exposure on caesiumated Si(100)2 × 1 surfaces (a) without steps and (b) with steps for various Cs deposition times (for a Cs flux of $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$): ●, 0 s; ×, 200 s; ○, 500 s; △, 1000 s.

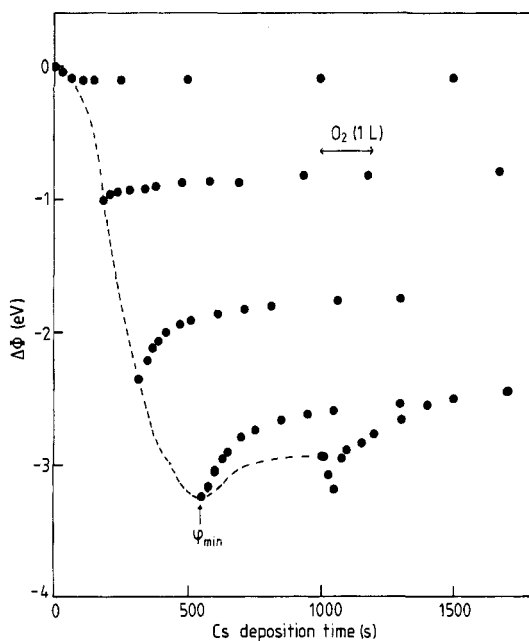


Figure 3. WF changes on O₂ adsorption on caesiumated Si(100)2 × 1 with steps (for a Cs flux of $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$): ---, WF change on Cs adsorption on clean stepped Si(100)2 × 1; ●, WF change on O₂ exposure, which increases along the x axis (the length of the arrow corresponds to 1 L).

corresponds to 1 L. This figure shows that, for Cs coverages up to the WF minimum Φ_{\min} , the adsorbed O causes an increase in the WF whereas, below Φ_{\min} , the WF initially decreases and subsequently increases with increasing O₂ exposure. Below Φ_{\min} , i.e. at low Cs coverages, O resides on both Cs-free areas and on top of Cs while, near saturation Cs coverage, O first resides underneath the Cs layer, causing lowering of the WF, and

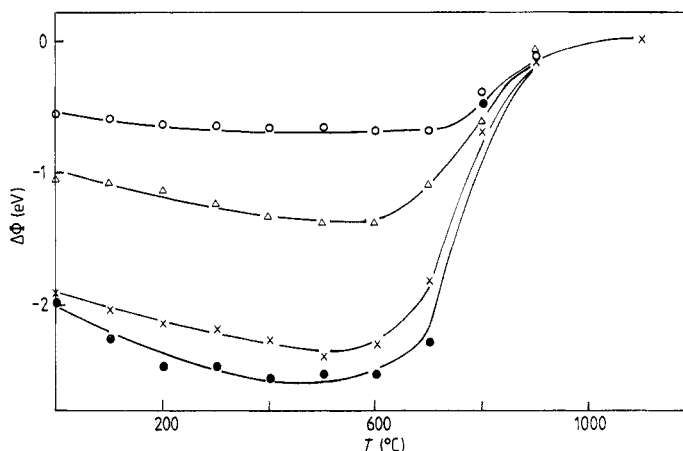


Figure 4. WF change against annealing temperature of caesiated stepped Si(100)2 × 1 surfaces (which had been exposed to 30 L of O₂) for various Cs deposition times (for a Cs flux of $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$): ○, 130 s; △, 300 s; ×, 500 s; ●, 1000 s.

subsequently on top of Cs. Similar results have been reported for O₂ adsorption on caesiated metals and other semiconductors [6–9]. The results for O₂ adsorption on caesiated Si(100)2 × 1 without steps (not shown) are similar with those in figure 3.

3.3.3. Heating effects. Figure 4 shows the change in WF plotted against annealing temperature of caesiated stepped Si(100)2 × 1 surfaces which were exposed to 30 L of O₂. For all Cs coverages, the WF initially decreases and subsequently increases. According to the TDS measurements in § 3.3.4, neither Cs nor O₂ is removed from the surface at temperatures below 300 °C. However, the WF starts to decrease right above room temperature. This suggests that the O₂ which is adsorbed on top of the Cs layer diffuses under the Cs, thus causing the lowering of the WF. Above 300 °C, Cs is removed first and this removal is more drastic above 600 °C. The repetition of the above measurements on Si(100)2 × 1 without steps did not give any different results.

3.3.4. TDS measurements. Figures 5(a) and 5(b) show the TDS spectra of SiO and Cs from stepped and flat caesiated surfaces of Si(100)2 × 1, respectively, which had been exposed to 4 L of O₂. The broken curves are the TDS spectra of a saturated Cs overlayer exposed to 4 L of O₂. As the amount of pre-adsorbed Cs increases, the SiO peak increases. The desorption of the oxide from the surface takes place at $T_s \geq 800 \text{ °C}$, almost after complete removal of Cs. The important information from figure 5 is that the areas under the corresponding SiO peaks are greater on Si(100)2 × 1 with steps than on the same surface without steps, as shown more clearly in the next figure.

Figure 6 shows the areas under the TDS peaks of SiO (shown in figure 5) plotted against the time of Cs pre-deposition from the flat and stepped Si(100)2 × 1 surfaces which were exposed to 4 L of O₂. The areas of SiO TDS peaks are proportional to the coverage of the oxide. According to previous reports [13, 19], similar TDS spectra of SiO have been attributed to a decomposition of SiO₂, ($\text{SiO}_2 + \text{Si} \rightarrow 2\text{SiO}$). This will be confirmed in § 3.4. Figure 6 shows that, for the same O₂ exposure, the amount of oxide increases almost linearly with increasing amount of pre-deposited Cs on both surfaces, with and without steps. This increase is greater on the stepped Si(100)2 × 1 surface. In

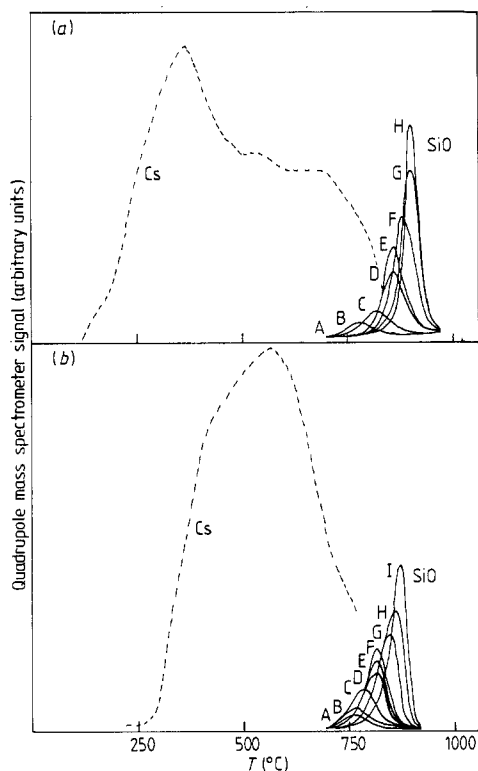


Figure 5. TDS spectra of SiO and Cs from (a) stepped and (b) flat caesiated surfaces of Si(100) 2×1 (which had been exposed to 4 L of O₂) for various Cs deposition times ($\beta = 13 \text{ K s}^{-1}$; Cs flux, $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$): curves A, 0 s; curves B, 100 s; curves C, 200 s; curves D, 300 s; curves E, 400 s; curves F, 500 s; curves G, 600 s; curves H, 800 s; curves I, 1200 s.

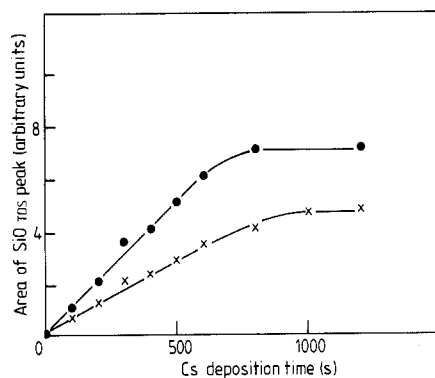


Figure 6. Areas under the TDS peaks of SiO (shown in figures 5(a) and 5(b)) against time of Cs pre-deposition from stepped (●) and flat (×) Si(100) 2×1 caesiated surfaces which had been exposed to 4 L of O₂ (for a Cs flux of $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$).

other words, for the same O₂ exposure, the amount of Si–O complex is greater on caesiated Si(100) 2×1 with steps than without steps. The curves in figure 6 are analogous to those of the ratio of Cs to Si Auger peak heights against Cs deposition time on Si(100) 2×1 with steps and without steps shown elsewhere [17]. This comparison implies that the amount of Si oxide on the surface depends on the coverage of pre-adsorbed Cs. The presence of steps increases the sticking coefficient and the maximum amount of Cs on Si(100) 2×1 while the adsorption of O₂ alone (§ 3.2) on clean Si(100) 2×1 is not affected substantially by the steps.

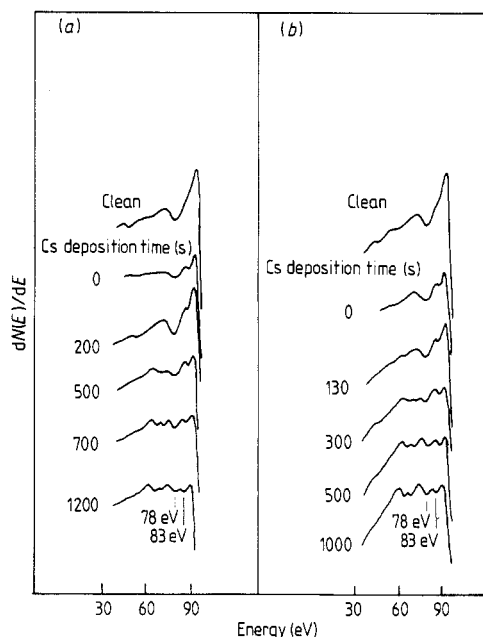


Figure 7. Low-energy Auger spectra of $\text{Si}(100)2 \times 1$ (a) with steps and (b) without steps after increasing caesiation, O_2 adsorption and subsequent heating to 800°C . (Cs flux, $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$; $E_p = 2 \text{ kV}$; 4 L of O_2).

3.4. Identification of the Si oxides

Figures 7(a) and 7(b) show the low-energy Auger spectra of $\text{Si}(100)2 \times 1$ surfaces without and with steps, respectively, on increasing degree of caesiation followed by exposure to O_2 and heating to 800°C . These figures show that, when the caesiated $\text{Si}(100)2 \times 1$ surface is exposed to 15 L of O_2 and subsequently heated to 800°C for about 30 s , the 78 eV and 83 eV Si peaks appear, which are characteristic of SiO_2 and SiO_4 , respectively [2]. Most probably the formation of the oxide takes place during the heating cycle which provides the activation energy for the oxidation reaction. These peaks increase with increasing amount of pre-deposited Cs and are larger on $\text{Si}(100)2 \times 1$ with steps than without steps. In other words, for the same time of Cs deposition and O_2 exposure, more oxide is formed on $\text{Si}(100)2 \times 1$ with steps than without steps. The results in figure 7 are consistent with attributing the observed TDS spectra of SiO to a decomposition of SiO_2 .

3.5. Repetition of the oxidation cycle

Figures 8(a) and 8(b) show the low-energy Auger spectra after increasing number of cycles of O_2 adsorption on Cs saturated $\text{Si}(100)2 \times 1$ surfaces without and with steps, respectively, and subsequent heating to 800°C . As seen in these figures, the 78 eV peak due to SiO_2 increases drastically with increasing number of oxidation cycles. The increase is such that it masks the 83 eV peak due to SiO_4 , which remains almost invariant on repeating the number of oxidation cycles. This is consistent with previously reported results [2]. The important information in this figure is that the increase in the 78 eV peak, due to SiO_2 , with increasing number of oxidation cycles is substantially greater on the stepped surface, as shown better in the next figure.

Figure 9 shows the variation in the SiO_2 film thickness with increasing number of oxidation cycles (shown in figure 8) on $\text{Si}(100)2 \times 1$ with and without steps. After six

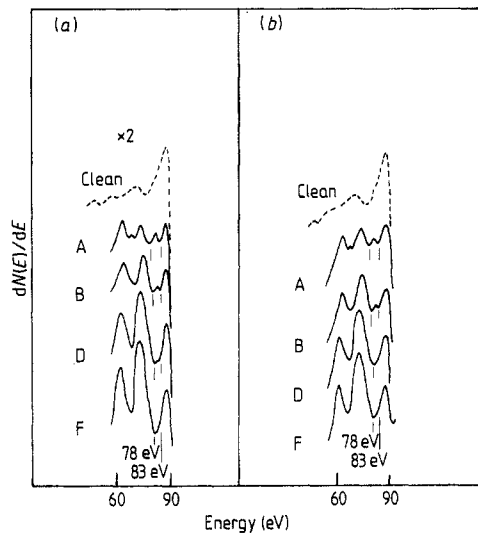


Figure 8. Low-energy Auger spectra after increasing number of cycles of room-temperature caesiation, O_2 adsorption and heating to $800^\circ C$ of $Si(100)2 \times 1$ surfaces (a) without and (b) with steps for various Cs deposition times: curves A, 0 s; curves B, 100 s; curves D, 300 s; curves F, 500 s.

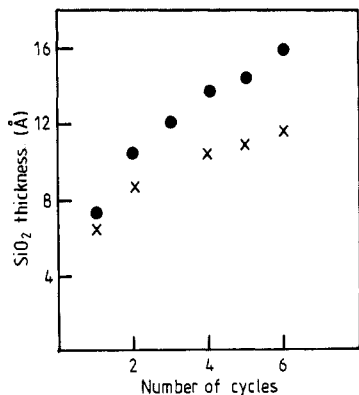


Figure 9. Variation in the SiO_2 film thickness with increasing number of oxidation cycles (shown in figure 8) on $Si(100)2 \times 1$ with and without steps.

oxidation cycles the thickness d of the oxides was 16 \AA and 11 \AA on $Si(100)2 \times 1$ with and without steps, respectively. The thickness d of the oxide was calculated from the following equation [2]:

$$I_{Si} = I_{Si}(0) \exp(-d/\lambda)$$

where $I_{Si}(0)$ and I_{Si} are the Auger peak heights of Si(92 eV) from the clean surface and the oxidised surface, respectively, and λ is the mean free path of electrons in SiO_2 and has been taken to be equal to 6.5 \AA [2]. From the slopes of the curves in figure 9, we may predict an increase in the oxide thickness with further increase in the number of oxidation cycles.

4. Conclusions

An experimental investigation of O_2 adsorption on caesiated $Si(100)2 \times 1$ surfaces with and without steps has been carried out in an UHV system by LEED, AES, TDS and WF

measurements. The purpose of this experiment was to study the effect of the steps on the oxidation of Si(100)2 × 1 surfaces in the presence of Cs. The presence of Cs on both surfaces increases the sticking coefficient and the maximum amount of O₂ that can be adsorbed on the surface. This increase is greater with increasing amount of pre-deposited Cs. At high Cs coverages, O is initially adsorbed under the Cs layer and subsequently resides on top of Cs. According to AES measurements, on exposure to O₂ of a Si(100)2 × 1 surface saturated with Cs and subsequent heating of the substrate to 800 °C, SiO₄ and SiO₂ are formed on the surface. For convenience, we call this the oxidation cycle. WF and TDS measurements suggest that, on heating, the O which is adsorbed on top of Cs diffuses under the Cs layer and forms oxides with the substrate. At 800 °C, Cs is removed completely while the oxide remains. Above 800 °C, SiO₄ and SiO₂ dissociate and desorb in the form of SiO. After one oxidation cycle, the growth of the oxide is greater on stepped than on non-stepped Si(100)2 × 1 surfaces. This is attributed to the higher saturation coverage of Cs on stepped Si. When the oxidation cycle is repeated several times, SiO₂ predominates and its average thickness increases with increasing number of oxidation cycles. For the same number of oxidation cycles, the thickness of SiO₂ is substantially greater on the stepped Si(100)2 × 1. For example, after the sixth oxidation cycle the average thicknesses d of SiO₂ are about 16 Å and 11 Å on Si(100)2 × 1 with and without steps, respectively.

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References

- [1] Tougaard S, Morgen P and Onsgaard J 1981 *Surf. Sci.* **111** 545
- [2] Derrien J and Commandre M 1982 *Surf. Sci.* **118** 32
- [3] Hollinger G and Himpfel F J 1984 *Appl. Phys. Lett.* **44** 93
- [4] Lewis E A and Irene E A 1986 *J. Vac. Sci. Technol. A* **3** 916
- [5] Franciosi A, Soukiassian P, Philip P, Chang S, Wall A, Raisanen A and Troullier N 1981 *Phys. Rev. B* **35** 910
- [6] Papageorgopoulos C A and Chen J M 1973 *Surf. Sci.* **39** 313
- [7] Papageorgopoulos C A 1982 *Phys. Rev. B* **25** 3740
- [8] Kennou S, Ladas S and Papageorgopoulos C A 1985 *Surf. Sci.* **164** 290
- [9] Papageorgopoulos C A and Chen J M 1975 *Surf. Sci.* **52** 53
- [10] Soukiassian P, Bakshi M H, Hyrych Z and Gentle T M 1987 *Phys. Rev. B* **35** 4176
- [11] Bakshi M H, Soukiassian P, Gentle T M and Hyrych Z 1987 *J. Vac. Sci. Technol. A* **5** 1425
- [12] Michel E G, Oelling E M, Asensio M C and Miranda R 1987 *Surf. Sci.* **189** + **190** 245
- [13] Papageorgopoulos C A, Foulis S, Kennou S and Kamaratos M 1989 *Surf. Sci.* **211** + **212** 991
- [14] Rajan V T and Falicov L M 1976 *J. Phys. C: Solid State Phys.* **9** 2533
- [15] Kennou S, Cherief N, Cinti R C and Nguyen T T A 1989 *Surf. Sci.* **211** + **212** 685
- [16] Kaplan R 1980 *Surf. Sci.* **93** 145
- [17] Kennou S, Kamaratos M, Ladas S and Papageorgopoulos C A 1989 *Surf. Sci.* **216** 462
- [18] Krueger S and Mönch W 1980 *Surf. Sci.* **99** 157
- [19] Liehr M, Jewis J E and Rublott G M 1987 *J. Vac. Sci. Technol. A* **5** 1559