The behaviour of Na on 1 × 1 and 7 × 7 structures of Si(111) and its effect on the oxidation of these structures

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Abstract. Deposition of Na on 1 × 1 and 7 × 7 structures of Si(111) at room temperature (RT) forms a uniform layer with a rather weak metallic character. The coverage of Na can be determined at any time of the Na deposition by a flux meter. The binding energy of Na is greater on a reconstructed 7 × 7 than on the 1 × 1 structure of a Si(111) surface. The initial dipole moment and the maximum $\Delta\phi$ are greater for Na on the 1 × 1 structure. Near saturation Na coverage, the oxygen goes initially under the Na layer forming a Na–O–Si complex and subsequently resides on top of it. The presence of Na on Si(111) causes a drastic increase of the initial sticking coefficient of oxygen by about ten times. When oxygen is adsorbed on Na-covered Si(111) surfaces at RT and the system is heated to 700 °C, Na is removed from the surface while oxygen forms SiO_4 and SiO_2. By repeating this cycle several times (seven) SiO_2 predominates and its average thickness is about 9 Å. However, this thickness is smaller than when Cs is used instead of Na. This indicates that Cs is more effective as a promoter of the oxidation. However, the oxide formation occurs at a lower temperature than with Cs additives. Finally, the effect of Na on the oxidation of Si was almost the same on the 7 × 7 and 1 × 1 structures of Si(111) surfaces.

1. Introduction

The promotion of oxidation of semiconductors with alkali additives is gaining increasing interest for the formation of SiO_2–Si interfaces, which are very useful for microelectronic devices [1–7]. Direct oxidation of Si requires relatively high temperatures (~1000 °C) and oxygen pressures (~1 atm) which make the formation difficult and limit the perfection of the interfaces. Therefore, it is more convenient to oxidize Si at lower temperatures and pressures. Our recent experimental results suggest that the presence of Cs on Si(111) surfaces causes an increase of the initial sticking coefficient of oxygen on the surface by about ten times. When oxygen is absorbed on Cs-covered Si(111) at room temperature and the system is subsequently heated to about 800 °C, Cs is removed from the surface and formation of SiO_2 takes place [8].

The reported studies on the enhanced oxidation of Si surfaces with alkali additives have been mainly concentrated on the large alkali atoms of Cs and K. A limited effort exists on a study of the small Na atom as a promoter of oxidation of Si. In the present work we study the behaviour of Na on 1 × 1 and 7 × 7 structures of Si(111) and subsequently the effect of Na on the oxidation of the above surfaces of Si.

2. Experimental procedure

The experiments took place in an UHV chamber with a base pressure of about 5×10^{-11} torr [9]. The study was performed with the following components: a hemicylindrical mirror analyser (HCMA) for Auger and Electron Energy Loss Spectroscopy (AES, EELS), LEED optics for the examination of the substrate and adsorbate order, a Quadrupole Mass Spectrometer for Thermal Desorption (TD) measurements and an extra electron gun for Work Function (WF) measurements. All Auger data were obtained with a 4 keV, 10 μA primary beam and a 10 V_{p-p} modulation voltage. The EELS measurements were made with a 105 eV, 10 μA primary electron beam and a 2 V_{p-p} modulation which results in an inflection width of the elastic peak of 1.5 eV. Spectroscopically pure O_2 was admitted to the system through a backable leak-valve. The partial pressure of O_2 during its admission was $1-5 \times 10^{-8}$ torr. Sodium was evaporated from a resistively heated dispenser (SAES Getters) source and the background pressure during Na deposition was below 10^{-10} torr. The Na flux was constant at $1 \pm 0.1 \times 10^{13}$ cm^{-2} s^{-1} and was measured by a surface ionization probe. The samples were heated by passing current through a 0.05 mm Ta strip uniformly pressed between the sample and a Ta-foil case. The specimen temperature, T_s, was measured by a NiCr/NiAl thermocouple spot-welded to the case and calibrated with an infra-red pyrometer in the 600 to 1000 °C temperature range. The main impurity of Si(111) was carbon which was removed by several cycles of Ar$^+$ sputtering with 500 eV and annealing at 850 °C. The carbon AES peak was 10^3 times smaller than the Si 92 eV peak. A quick cooling of the Si(111) sample from 1000 °C to RT produced a '1 × 1' surface structure, while a slow gradual decrease of T_s at a cooling rate of ~4 K s^{-1} produced a 7 × 7 surface structure [8].

3. Results

3.1. Na on Si(111) surfaces

3.1.1. LEED and AES measurements. The understanding of the effect of Na on the oxidation of Si requires knowledge of the behaviour of Na alone on the Si(111) surfaces.

Adsorption of Na on clean 1 × 1 and 7 × 7 structures of Si(111) does not produce any extra LEED pattern.

Figure 1 shows the curves of Auger peak heights of Na(995 eV) and Si(92 eV) versus Na deposition time on 1 × 1 and 7 × 7 structures of Si(111). Initially, the Na(995 eV) peaks increase and the Si(92 eV) peaks of the substrate decrease linearly up to about 100 s of Na deposition where all curves form a break. After this break the slopes of the Auger curves are smaller. At 200 s a second break appears and the slopes decrease even more and tend to form a plateau. As it is seen in this figure the variations of the above peaks are about the same for Na deposition on both 1 × 1 and 7 × 7 structures of Si(111).

3.1.2. WF measurements. Figure 2 shows the WF change versus Na deposition time on 1 × 1 and 7 × 7 structures of Si(111). The WF value of a clean 7 × 7 structure is 0.20 eV greater than that of the 1 × 1 structure. The initial drastic decrease of the WF with increasing deposition of Na on Si(111) surfaces is a characteristic behaviour of alkali metals on metallic and semiconductor surfaces [6, 10–13]. The important feature of these curves is the knee, i.e. the abrupt increase of the WF change near 100 s of Na deposition. It is noteworthy that the knees of the WF curves almost coincide with the first break of the Si Auger curves in figure 1.
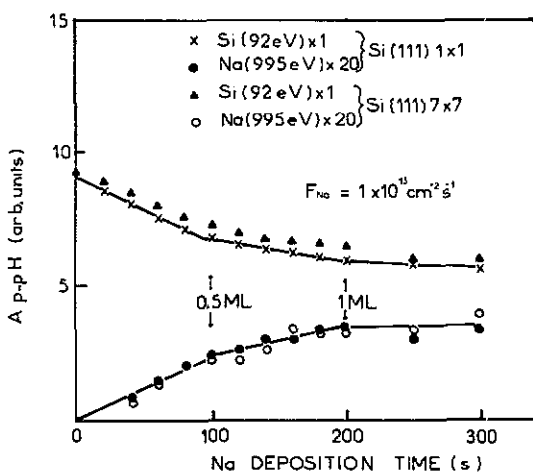
Figure 1. Auger peak height of Na(995 eV) and Si(92 eV) versus Na deposition time on '1 × 1' and 7 × 7 structures of Si(111).
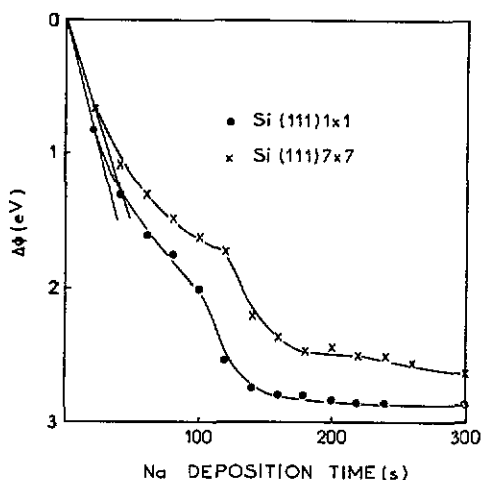

Figure 2. WF change versus Na deposition time on '1 × 1' and 7 × 7 structures of Si(111).

The initial slope of the WF curve and final value with Na deposition are greater on the 1 × 1 structure (2.7 eV) than on the 7 × 7 (2.5 eV) of Si(111). It is well known that the initial slope of the WF curve is proportional to the surface dipole moment. Thus, the initial dipole moment of the Na on the 1 × 1 structure is greater than that on the 7 × 7. This may be attributed to the fact that the 1 × 1 structure is more uniform than the reconstructed 7 × 7 structure and the average dipole length of Na on the 1 × 1 is greater. This is consistent with the following results, that the maximum WF increase of 0.16 eV for oxygen adsorption on a 7 × 7 structure is smaller than that measured for O_2 on the (1 × 1) structure (0.22 eV).

3.1.3. TDS measurements. Figure 3 shows the TD spectra of Na on Si(111) 1 × 1 surfaces. The heating rate β was 16 K s^{-1}. As is seen in this figure, there are three desorption
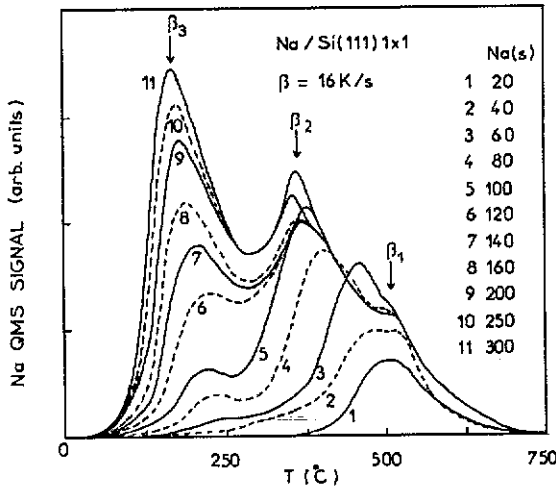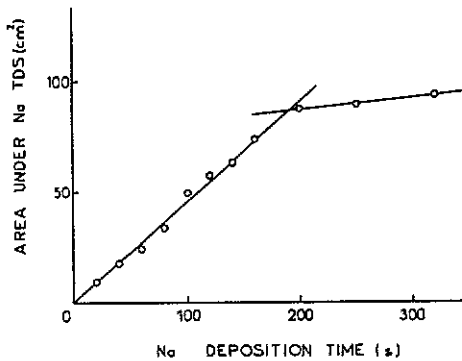
Figure 3. TD spectra on Si(111) 1 × 1 surfaces.

Figure 4. Area under the Na TD spectra of figure 3 versus deposition time.

peaks, β_1, β_2 and β_3. The low coverage β_1 peak appears at about 440 °C. The β_2 peak shifts substantially to lower energies with increasing Na coverage. Also, the low-energy peak β_3, which appears in the region of 100 °C, shifts to lower energies with increasing amount of deposited Na. The development of this peak occurs near 100 s where the first break of the Auger curves and the WF knee appear (figures 1 and 2). The TD spectra of Na on Si(111) are quite similar to those of alkali metals on metallic and most semiconductor surfaces [14, 15]. They extend over a wide range of temperatures, in contrast to the case of the sharp TD peaks which are due to formation of clusters or ionic bonding of the adsorbate to the substrate. The TD spectra of Na on Si(111) 7 × 7 are quite similar to those on Si(111) 1 × 1, except that the three peaks appear at higher temperatures on the 7 × 7 structure. This means that the binding energy of Na on the reconstructed 7 × 7 structure is greater than that on the 1 × 1 structure of the Si(111) surface. This is consistent with a smaller average dipole length of Na adsorbates on the 1 × 1 structure.

Figure 4 shows the area under the Na TD spectra of figure 3 versus Na deposition time. As is seen in this figure, the curve is roughly linear up to 200 s and above this
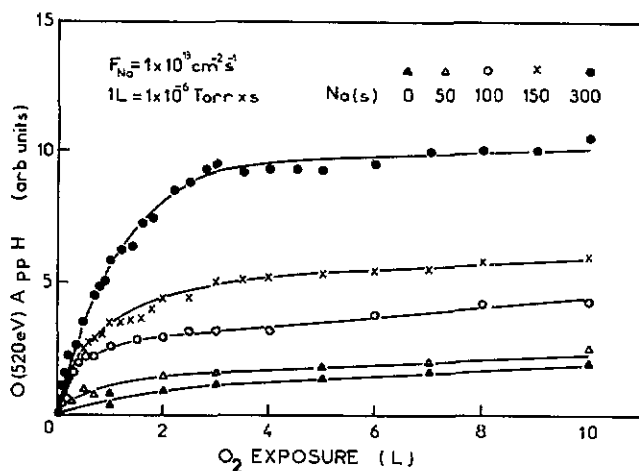
Figure 5. Auger peak height of O(520 eV) versus oxygen exposure on Na-covered Si(111) 1 × 1 surfaces.

deposition time the slope changes substantially. This curve is very interesting because a comparison with the Auger curves in figure 2 leads to very important information concerning the mechanism of Na adsorption on the clean Si(111) surface. For constant heating rate, the area under the TD spectra is proportional to the coverage of the adsorbate. A constant slope of this area versus deposition time implies that the sticking coefficient of the adsorbate is also constant.

3.2. O_2 on clean Si(111) surfaces

Although the behaviour of O_2 on Si(111) has been reported [8] it is convenient to mention the results briefly. Adsorption of O_2 at RT on 1 × 1 and 7 × 7 structures of Si(111) forms islands of SiO_4 which coexist with chemisorbed oxygen. The formation of the SiO_4 is concluded from the appearance of an Auger peak at 83 eV in agreement with [16]. We also found that the maximum WF increase of oxygen on the 7 × 7 structure of Si(111) is 0.16 eV which is smaller than 0.22 eV measured for O_2 on the (1 × 1) structure.

3.3. O_2 on Na-covered Si(111) surfaces

3.3.1. LEED observations. Adsorption of O_2 on Na-covered 1 × 1 and 7 × 7 structures of Si(111) surfaces does not produce any extra LEED pattern.

3.3.2. AES measurements. Figure 5 shows the Auger peak height of O(520 eV) versus oxygen exposure on Na-covered Si(111) 1 × 1 surfaces. Both the slope of these curves and the O(520 eV) peak height, for a certain O_2 exposure, increase substantially with an increasing amount of preadsorbed Na. For a nearly saturated Na layer the initial slope is about ten times greater than that without Na. Thus, the presence of a saturated Na layer on Si(111) 1 × 1 causes an increase of the initial sticking coefficient of O_2 on the surface by about ten times, while for 10 Langmuirs of O_2 exposure the O(520 eV) peak height is about five times greater than that without Na on the surface. The results on the 7 × 7 structure are quite similar.
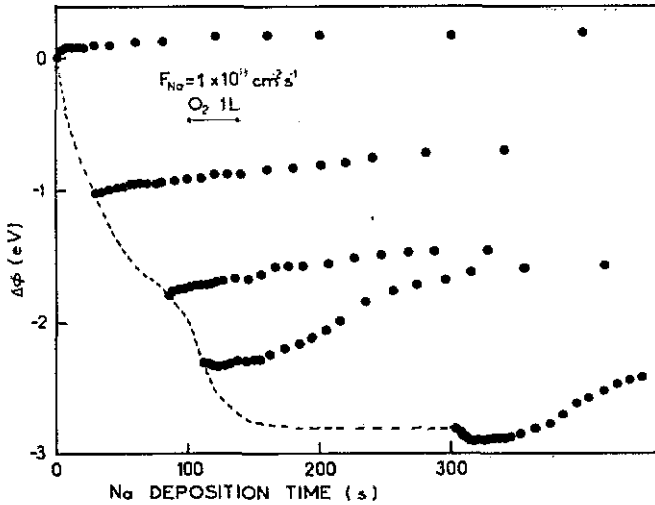
Figure 6. (i) WF change versus time of Na deposition on clean Si(111) 1 × 1 at RT (broken curve); and (ii) WF change versus O_2 exposure on Si(111) 1 × 1 precovered with different amounts of Na.
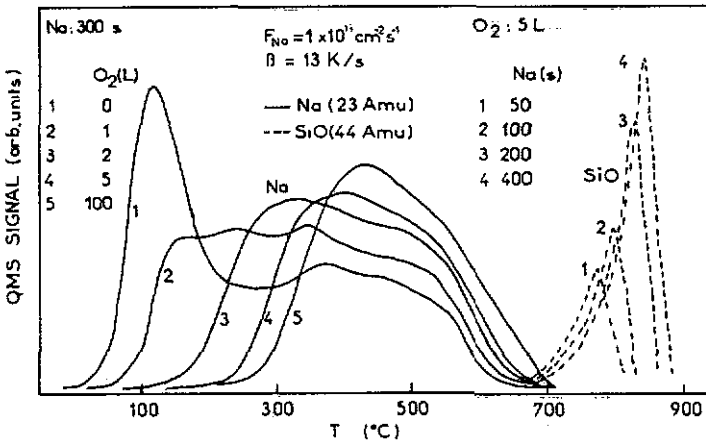

Figure 7. Full curves: TD spectra of Na after O_2 adsorption on nearly saturated Na layer. Broken curves: TD spectra of SiO after the exposure of different Na coverages on Si(111) 1 × 1 to 5 litres of oxygen.

3.3.3. WF measurements. Figure 6 shows (i) the WF change ($\Delta\phi$) versus time of Na deposition on clean Si(111) 1 × 1 at RT (broken curve) and (ii) the WF changes versus O_2 exposure on Si(111) 1 × 1 surfaces with different amounts of Na. Adsorption of O_2 on clean Si or Si covered with small amounts of Na, below the knee, causes a small increase of the WF of the surface. After the knee, the WF initially decreases and subsequently increases.

3.3.4. TDS measurements. The full curves in figure 7 show a series of TD spectra of Na after O_2 adsorption on Si(111) 1 × 1 which was precovered with a nearly saturated Na
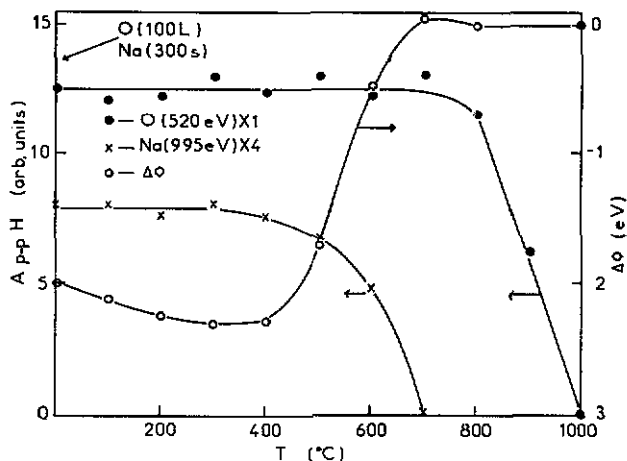
Figure 8. WF change and Auger peak heights of Na(995 eV) and O(520 eV) versus temperature T, of a Si(111) 1 × 1 surface which was Na-covered and subsequently exposed to 100 litres of O_2.

layer. The heating rate was 13 K s^{-1}. As is seen in figure 7, increasing the amount of oxygen on the Na/Si surface causes (a) a drastic decrease of the low energy TD Na peak (100 °C); (b) a sharpening (decrease of width) of the Na peak; and (c) a shift of the Na peaks to higher energy, while the complete desorption of Na from the Si(111) 1 × 1 surface occurs at about the same temperature (700 °C) independent of the amount of oxygen.

The broken curves in figure 7 show a series of TD spectra of SiO after the exposure of different Na coverages on Si(111) 1 × 1 to 5 Langmuirs of oxygen. According to this figure, SiO desorbs above 700 °C. The area under the spectra increases with an increasing amount of preadsorbed Na. TD peaks for the atomic masses which correspond to O_2, SiO_2, SiO_4, have not been measured. It is noteworthy that the spectra of SiO are sharp and their peaks shift to higher energies with an increasing amount of preadsorbed Na. Repetition of the above measurements on the Si(111) 7 × 7 substrate produces similar results. It appears that, after the coadsorption of Na and O_2, Na desorbs at 700 °C while oxygen desorbs mainly in the form of SiO at 800 °C, above the comlete removal of Na. These results are quite similar to those of Cs + O_2 on Si(111) surfaces [8].

3.3.5. Heating effects. Figure 8 shows the WF change and Auger peak heights of Na(995 eV) and O(520 eV) versus temperature T of a Si(111) 1 × 1 surface which was Na-covered and subsequently exposed to 100 Langmuirs of O_2. Initially, the WF decreases to a minimum value, then subsequently increases. As the predeposited amount of Na increases the initial decrease is larger. The initial WF lowering could be attributed to the diffusion of an oxygen overlayer under the Na layer. According to the AES measurements (figure 8) Na is completely removed at about 700 °C while the oxygen remains on the surface. As will be shown in the following paragraph, the oxyen which remains on the surface at $T_s = 700$ °C is in an Si-oxide form.

Figure 9 shows a series of EELS spectra of Si(111) 1 × 1 covered with Na and O_2 and subsequently heated at different temperatures. The clean surface shows the characteristic loss peaks of Si [17]. After Na deposition a new peak appears with an energy
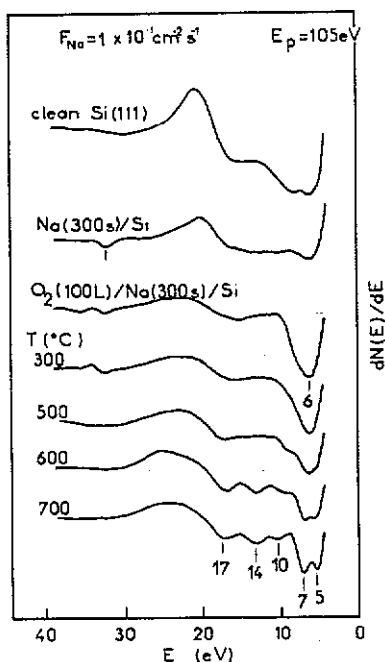
Figure 9. A series of EELS of Si(111) 1 × 1 covered Na and O_2 adsorbates and subsequently heated at different temperatures.

~31 eV which is attributed to the Na 2p level. During O_2 exposure a broad peak with an energy of about 6 eV is developed. This peak is attributed to the O 2p level. With increasing temperature above 500 °C, the 6 eV loss peak is split into two peaks of 5 and 7 eV. In addition, three new peaks appear at 10, 14 and 17 eV. All these peaks are characteristic of the Si–O bond [16]. After 800 °C the intensity of these peaks decreases and at 1000 °C the spectrum of the clean Si reappears.

Figure 10 shows low-energy Auger spectra of clean and Na + O_2-covered Si(111) 1 × 1 which is subsequently heated to 700 °C. The 83 eV and 78 eV Auger peaks are characteristic of SiO_4 and SiO_4, respectively [16]. The observed TD spectrum of SiO (figure 7) is a product of dissociation of the above oxides. The above heating results are quite similar for the Si(111) 7 × 7 substrate.

4. Discussion

4.1. Na on clean Si(111) surfaces

As is mentioned in section 3.1.1., figure 4 suggests that the sticking coefficient of Na on a Si(111) surface is constant up to 200 s of Na deposition. If we assume that the initial sticking coefficient of Na on Si(111) surfaces is equal to 1 (one) and we know the value of the Na flux, we may calculate the Na coverage at any time of Na deposition, which is given by:

$$\Theta_{Na} = \frac{S F_{Na} t_{Na}}{N_{Si(111)}}$$

where S is the sticking coefficient, F_{Na} is the Na flux which has a constant value of
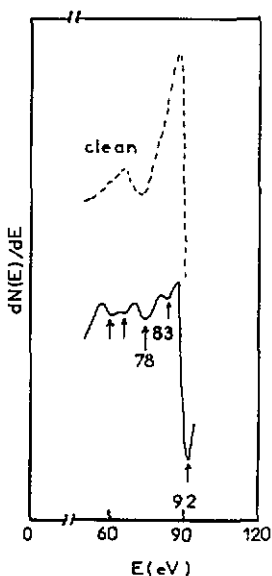
Figure 10. Low-energy Auger spectra of clean and Na + O_2 covered Si(111) 1 × 1, subsequently heated to 700 °C.

$(1 \pm 0.1) \times 10^{13}$ cm^{-2}s^{-1}, t_{Na} is the time of Na deposition and $N_{Si(111)}$ is the density of the top-most layer of the Si(111) surface which is equal to 2×10^{15} atoms cm^{-2}. From the above equation we may calculate the coverages: (a) at the first break point (100 s) of the Auger curves in figure 1, $\Theta_{Na} \approx 0.5$; (b) at the second break (200 s), $\Theta_{Na} \approx 1$. Above 200 s the slope of the curves, in figures 1 and 4, decreases substantially. This decrease is attributed to the growth of a second layer where Na is adsorbed with a sticking coefficient of 0.13. As is seen in figure 2, the $\Delta\phi$ versus Na deposition time curves exhibit a knee before the final formation of the plateau, which coincides with the first break of the Auger curves (figure 1). Similar knees have been reported for alkali metals on Si(100) surfaces [13, 15]. It appears that this knee is a general property of alkali metals, at least, on Si(111) and Si(100) surfaces. The knee is due to an abrupt decrease of the WF which resulted from an increase of the average dipole moment. We may consider two possible views to explain this knee.

(i) The alkali adatoms form clusters from the early stages of deposition. At certain coverage, $\Theta \approx 0.5$, there is an interaction between the neighbouring clusters leading to a more uniform distribution of the alkali atoms. The consequence of this is the abrupt increase in dipole moment. According to a related model, clustering of adsorbed atoms causes a decrease of the mean dipole moment per atom [18, 19]. However, this view does not quite agree with the Auger measurements (figure 1). The change from clustering to a more uniform distribution of the adatoms should increase and not decrease the slope of the Auger curve, as happens in figure 1 [20].

(ii) Above $\Theta = 0.5$ the alkali atoms must reside on different sites, which leads to displacements of the adatoms in such a way as to increase the average dipole moment and cause an additional decrease of the WF.

The wide TD spectra of Na on Si(111) surfaces and the low-energy peak (β_3) in figure 3 support the metallization of the Na layer at high coverages.

4.2. O_2 on Na-covered Si(111) surfaces

According to AES measurements (figure 5) the presence of Na causes an increase of both the initial sticking coefficient and the maximum amount of the subsequently adsorbed oxygen.

The WF measurements (figure 6) suggest that, at low Θ_{Na}, oxygen atoms are deposited on both Na-free and Na-covered areas of the Si substrate resulting in an increase of the WF. However, at high Θ_{Na}, initially oxygen atoms go below the Na layer. Most likely, the O_2 molecules undergo dissociative chemisorption on top of the Na layer and subsequently the oxygen atoms are bound between the Si and Na forming a Si–O–Na complex. At this stage we cannot preclude any Na-oxide formation. After the completion of a fractional or one underlayer the oxygen atoms reside on top of the Na layer. Upon subsequent heating of the surface the WF initially decreases (figure 8), which indicates that the heating provides the activation energy for further diffusion and interaction of oxygen.

TDS measurements (figure 7) suggest that the presence of oxygen on Na-covered Si(111) causes the diminishing of the low-energy TD peak, β_3, which is attributed to the metallic character, and the narrowing of the TD Na spectra. In other words the presence of oxygen causes the demetallization of the Na layer. The Na is removed at 700 °C and oxygen is mainly desorbed at ~800 °C in the form of SiO. For the same coverage of O_2, the area of the SiO TD spectrum increases with increasing amount of predeposited Na. EELS (figure 9) and low-energy Auger (figure 10) spectra measured after heating the Na + O/Si(111) system at 700 °C, i.e. after completely removing Na from the surface, indicate that oxygen forms SiO_2 and SiO_4 compounds (figure 3). With further heating these compounds desorb as SiO.

The thickness of the Si-oxide was calculated from the equation

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

where $I_{Si}(0)$ and I_{Si} are, respecively, the Auger peak heights of Si(92 eV) from clean and after heating the Na-covered Si(111) 1×1 surfaces to 700 °C and which were exposed to 10 Langmuirs of O_2; d is the average thickness of the oxide and λ is the mean free path of electrons in the oxide which has been taken as $\lambda \approx 6.5$ Å [16] including the analyser geometrical factor. It has been found that $d = 4$ Å. Repetition of the above cycle, O_2 (10 Langmuirs) plus Na (1 ML)/Si(111) plus heating at 700 °C seven times, causes the SiO_2 to predominate, as is indicated from the growth of the 78 eV AES peak, and $d = 9$ Å. This thickness is substantially smaller than that when, instead of 1 ML of Na, we use 1 ML of Cs, indicating that Cs is more effective as a promoter of oxidation. However, the complete removal of Na and the oxide formation occurs at about 100 °C lower than with the Cs additive. Finally, the effect of Na on oxidation of Si was almost the same on 7×7 and 1×1 structures of the Si(111) surfaces.

5. Summary

Deposition of Na on 1×1 and 7×7 structures of Si(111) at RT forms a uniform layer with a rather weak metallic character. The coverage of Na can be determined at any time of Na deposition with a flux meter. Above $\Theta = 0.5$ the Na atom resides on different sites and the deposition of Na is continuous after the completion of the first layer but with about a ten times smaller sticking coefficient. The binding energy of Na is greater

on the reconstructed 7 × 7, than on the 1 × 1 structure, of Si(111) surface, while the initial dipole moment and the maximum WF change during Na deposition are greater on the 1 × 1 structure.

Adsorption of oxygen on a Na-covered Si(111) surface diminishes the metallic character of the Na layer. Near saturation Na coverage, the oxygen goes initially under the Na layer forming a Na–O–Si complex and subsequently resides on top of it. Heating provides the activation energy for further diffusion.

The presence of Na on Si(111) causes a drastic increase of the initial sticking coefficient of oxygen by about ten times and of the maximum amount of oxygen that can be deposited on the surface. When oxygen is adsorbed on Na-covered Si(111) surfaces at RT and the system is heated at 700 °C, the Na is removed from the surface while the oxygen forms SiO_4 and SiO_3 with an average thickness of about 4 Å. By repeating this cycle seven times the SiO_2 predominates and its average thickness is close to 9 Å However, this thickness is smaller than when instead of 1 ML of Na 1 ML of Cs was used. This indicates that Cs is more effective as a promoter of oxidation; however, Na is completely removed from the Si(111) surfaces and the oxide formation occurs at lower temperatures than with Cs additives.

Finally, the effect of Na on the oxidation of Si was almost the same on 7 × 7 and 1 × 1 structures of Si(111) surfaces.

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