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Na-induced (7×7)-to-(3×1) structural transformation on a Si(111)7×7 surface and the resulting passivation of the surface towards interaction with oxygen

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Auger-electron spectroscopy, electron-energy-loss spectroscopy, low-energy electron-diffraction, and thermal-programmed-desorption measurements were performed in order to characterize the effect of small amounts of Na on the Si(111) surface structure and reactivity towards oxygen. We have observed a passivation effect of Na with respect to the oxygen adsorption rate and surface oxidation in the case when Na induces a (7×7)-to-(3×1) structural transformation of the initial Si(111)7×7 surface.

Over the past decade the structure and properties of metal-silicon interfaces have been of great technological and fundamental interest.[1-3] The changes in the chemical properties and reactivity of silicon surfaces induced by the presence of metals are determined by three main factors: (i) the kind of metal, (ii) the type of metal-silicon bonding, and (iii) the possible metal-induced reconstruction of the silicon surface, etc.[4-10] Undoubtedly, the factors (ii) and (iii) contribute to alterations in the density of the surface dangling bonds.[11-15] Irrespective of the extensive studies dedicated to alkali-metal modification effects leading to an increase of the oxygen adsorption rate and promotion of Si oxidation, no attention has been paid to the influence of possible alkali-metal-induced structural transformation of the Si surface on its chemical properties and reactivity.

This paper shows that the deposition of a certain amount of Na which induces a (7×7)-to-(3×1) structural transformation of the Si(111)7×7 surface can cause a passivation of the surface with respect to the interaction with oxygen. An advantage of the present system is that the Na-driven reconstriction is an activated process, so that it is favored only at elevated temperatures. Thus, we were able to perform a comparative study on the reactivity with respect to oxygen of both surfaces [Na/Si(111)7×7 and the Na/Si(111)3×1] covered with the same amount of Na.

The studies were carried out in a UHV apparatus equipped with a cylindrical mirror analyzer [used for Auger and electron-energy-loss spectroscopy (EELS) measurements] a two-grid, low-energy electron diffraction (LEED) system and a quadruple mass spectrometer [used for thermal programmed desorption (TPD) measurements]. The Si(111) wafers were cleaned by several cycles of Ar-ion bombardment and annealing at 1200 K, followed by a slow cooling to room temperature. After these procedures the impurity level of contaminants such as C and O falls below 0.01 monolayer and a sharp 7×7 LEED pattern is observed. The sample temperature was measured by a Pt/Pt− 10 at. % Rh thermocouple spot welded on a small Ta clip attached at the end of the Si crystal. Optical and ir pyrometers were used for calibration of the crystal temperature. Na was deposited on the surface from a well out-gassed SAES getter. The relative Na coverage was calibrated against the Na coverage corresponding to saturation of the first overlayer achieved upon Na adsorption on a Si(111)7×7 surface at 300 K (assigned conveniently as unity). Data obtained by parallel Auger-electron spectroscopy, work function, and TPD measurements were used for this calibration purpose. The Auger measurements were always performed in different spots after each exposure of Na or O_2 in order to prevent electron beam effects on the kinetic data. Oxygen coverage was calibrated on the basis of (i) the O(*KLL*)-to-Si(*KLL*) Auger peak-to-peak ratios and (ii) the areas under the SiO TPD spectra which are directly proportional to the absolute oxygen coverage. We assigned to unity the oxygen coverage achieved after ~3000 L (1 L = 10^{-6} torr s) oxygen exposure on Si(111)7×7 at 300 K when the rate of the oxygen uptake becomes extremely slow. By a coincidence the O(*KLL*)-to-Si(*KLL*) Auger peak-to-peak ratio for this oxygen exposure also equals 1. More details on the experimental procedure can be found in Refs. 13 and 14.

Room-temperature Na deposition on a Si(111)7×7 surface results in a gradual disappearance of the initial 7×7 pattern which is replaced by a 1×1 LEED pattern at completion of the first Na overlayer. The (7×7)-to-(3×1) reconstruction is an activated process and requires a critical Na coverage. The temperature range favoring the Na-induced (7×7)-to-(3×1) structural transformation was found to be $600 < T_S < 780$ K. The upper temperature limit is related to the fact that a further increase of T_S leads to a drop of the Na equilibrium coverage below that required for driving the reconstruction (at the Na deposition rates of 8×10^{12} atoms/s used in this study). The lower temperature limit is above the Na desorption temperature from Si(111)7×7 for Na coverages required to produce the structural change (see the TPD spectra in Fig. 2 below). That is why a procedure of Na adsorption at 300 K and subsequent heating failed to induce reconstruction. The latter occurs only when the Na dosing is carried out in the above-mentioned temperature range. By comparing the area under the TPD curves

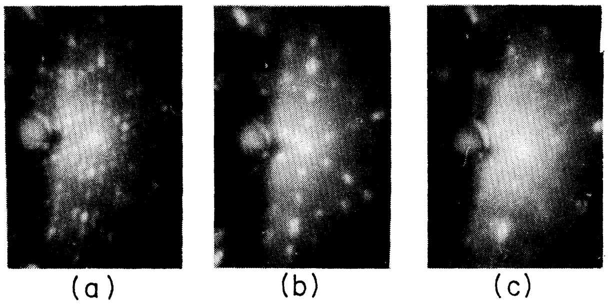

FIG. 1. LEED patterns of (a) a clean Si(111)7×7 surface; (b) a Si(111) surface after Na-induced 3×1 reconstruction; (c) a Si(111) surface after desorption of Na from (b) by heating to 920 K. $E_p = 90$ eV.

corresponding to completion of the first layer in Si(111)7×7 and the area under the Na TPD peak corresponding to the most "perfect" (3×1) order achieved upon Na deposition at 650 K we found that the optimum Na coverage stabilizing the (3×1) order is ~0.1 of the saturated first Na overlayer at 300 K. This dosing procedure and optimal Na coverage are used in the present study.

Figure 1 shows LEED patterns for a clean Si(111)7×7 surface, a Na reconstructed Si(111)3×1 surface, and a surface after Na desorption from Na/Si(111)3×1 by a linear heating to 920 K. The LEED data indicate that the initial 7×7 order is only partially restored after this relatively mild heating procedure. A complete resotration of the initial 7×7 order requires a prolonged annealing at ~1100 K.

Our TPD and EELS studies of the Na/Si(111)7×7 and Na/Si(111)3×1 surfaces have shown that the Na-induced structural transformation causes a substantial change in the Na TPD and EEL spectra. They are illustrated in Fig. 2 and can be summarized as follows.

(1) The Na TPD spectra from Na/Si(111)7×7 and Na/Si(111)3×1 for the same amount of deposited Na differ substantially in shape and temperature. As can be seen in Fig. 2(b) (TPD curves 2 and 3), Na desorption from Na/Si(111)3×1 occurs at higher temperature and is characterized by a rather narrow peak with a sharp leading edge. The desorption of Na is accompanied by a partial restoration of the 7×7 surface order, as indicated by parallel LEED measurements. Similar shapes of the desorption spectra were reported in most cases when the desorption process is accompanied by restructuring within the surface layer.[16–18] It has been established that the steep leading edge and the desorption curves are due to the decreasing of the desorption energy with decreasing adsorbate coverage because the desorption process is accompanied by a transition of the system to an energetically less favorable state. In the framework of this model

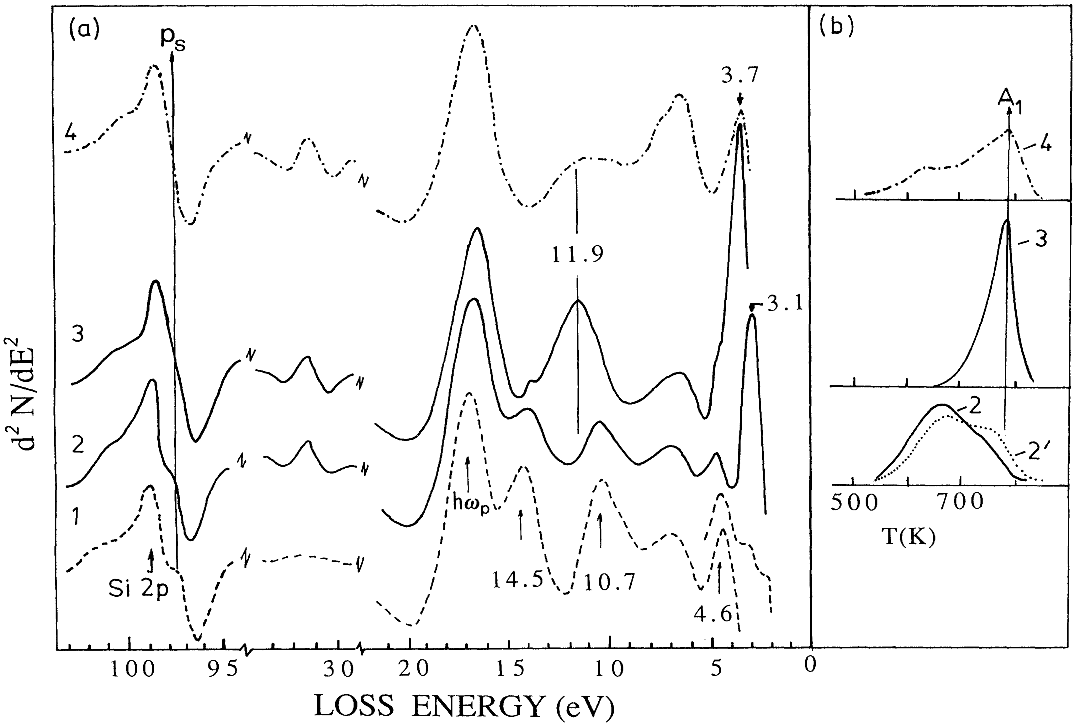

FIG. 2. (a) EEL spectra of 1, a clean Si(111)7×7 surface; 2, a 0.1 Na/Si(111)7×7 surface; 3, a 0.1Na/Si(111)3×1 surface; 4, after exposure of the 0.1 Na/Si(111)3×1 surface to 3000-L oxygen at 300 K. $E_p = 90$ and 250 eV. (b) Na TPD spectra from 2, 0.1Na/Si(111)7×7; 2′, 0.1Na+0.3O/Si(111)7×7; 3′, 0.1Na/Si(111)3×1; 4, 0.1Na+0.3O/Si(111)3×1. $dT/dt = 2$ K/s.

the Na TPD data in the present study indicate that the (7×7)-to-(3×1) transformation creates adsorption sites, characterized by a higher Na-Si binding energy. (2) In accordance to the TPD data, the Na/Si(111)3×1 surface is characterized by a different EEL spectrum, as illustrated in Fig. 2(b). Since detailed interpretation of the Si(111)7×7 loss features is given in Ref. 19 here only the induced changes will be considered. Comparison of the valence loss spectra reveals that (i) the room-temperature Na deposition causes only attenuation of the Si losses associated with back bond surface states (at 14.5 eV) and surface plasmons (at 10.8 eV) (Ref. 19) accompanied by an appearance of a Na-related peak at 3.1 eV (due to excitations involving the Na 3s valence states or interface Na $3s-\mathrm{Si}\,\pi$ states),[13] while (ii) the 650-K deposition leading to a $7\times7\Longrightarrow3\times1$ transformation results in an appearance of a rather intensive new feature at 11.9 eV accompanied by a complete removal of the 14.5-eV loss and an arising of a more intensive Na-induced peak located at a higher energy (3.7 eV). A difference also is observed in the Si 2p core-level spectra, where the Na-induced structural transformation leads to removal of the transitions at 99.3 eV (labeled as p_s) involving an empty dangling-bond surface level as a final state.[19] This p_s loss can be distinguished up to about 5 times higher Na coverages on a Si(111)7×7 surface.

The features in the loss spectra of the Na/Si(111)3×1 surface show that substantial changes occur in the surface band structure due to the Na-induced structural transformations. The fact that the appearance of a new loss peak at 11.9 eV is accompanied by the removal of the empty dangling-bond surface states can be used as an indication that the origin of the 11.9-eV feature lies in the formation of Si—Si bridge bonds as a result of the Na-induced structural changes. Another alternative explanation is that the 11.9-eV peak is related to transitions involving Si—Na bonds which differ from the usual Na—Si absorption bonds observed in the cases when no reconstruction occurs. In both cases the 11.9-eV feature reflects the surface properties of the system and, as will be discussed below, it is significantly affected by adsorption of oxygen. However, a definite assignment of the 11.9-eV feature requires more in depth inverse photoemission spectroscopy and/or angle-resolved ultraviolet photoemission spectroscopy studies of this system.

Room-temperature oxygen adsorption on a Na/Si(111)3×1 surface causes smearing of the LEED patterns and an increase of the background intensity, although diffuse and weak $\frac{1}{3}$ order spots can be distinguished even after oxygen exposure of 3000 L when the O(KLL)-to-Si(KLL) Auger ratio becomes 0.6. The LEED data for an oxygen-induced partial destruction of the 3×1 order are confirmed also by the parallel changes in the Na TPD spectra where a lower-temperature Na desorption peak arises at the expense of the A_1 peak characteristic for a "perfect" (3×1) order [see Fig. 2(b), curve 4]. Here, it is worthwhile to remember that this effect of oxygen adsorption on the Na TPD spectra is opposite to that observed for Na/Si(111)7×7. In the latter system oxygen coadsorption leads to stabilization of the Na absorption state, as judged from the development of a higher-temperature feature in the Na TPD spectrum [curve 2′ in Fig. 2(b)]. Obviously, in the case of Na/Si(111)3×1 the stabilization effect of oxygen cannot compensate that of the (3×1) order. As predicted above, oxygen adsorption also removes the new loss feature at 11.9 eV and suppresses the Na-induced loss at 3.7 eV [see loss spectrum 4 in Fig. 2(a)].

Figure 3 presents the oxygen uptake curves for clean Si(111)7×7, 0.1Na/Si(111)7×7, and 0.1Na/Si(111)3×1 surfaces. The most surprising result is that despite the presence of Na, which is well known as a very efficient promoter of the oxygen adsorption, the reactivity of the 0.1Na/Si(111)3×1 surface falls far below that of a Na-free Si(111)7×7 surface, while the same amount of Na results in substantial promotion of the reactivity of a Na/Si(111)7×7 surface. This result indicates that the Na-induced $(7\times7)\Longrightarrow(3\times1)$ structural transformation leads to passivation of the surface which cannot be compensated by the promoting effect of Na. The magnitude of this passivation effect is determined by the degree of "perfectness" of the induced new surface order, as can be judged by the oxygen uptake curves obtained for "perfect" and less "perfect" Na/Si(111)3×1 surfaces with the same Na coverage (curves 3 and 3′ in Fig. 3). By comparing the oxygen coverages achieved after 3000-L O_2 absorption at 300 K we have established that the capacity of the 0.1Na/Si(111)3×1 surface for oxygen absorption is also reduced down to 0.6 compared to 1 for a Na-free Si(111)7×7 surface.

The major factor supposed to determine the reactivity of Si surfaces is the density of the surface dangling bonds. This density depends on the actual Si surface order, the degree of roughness of the surface and the presence of adsorbates.[20–23] For example, a cleaved Si(111)2×1 surface characterized by a smaller density of dangling bonds than Si(111)7×7 exhibits a lower activity towards oxygen. As has been reported in Ref. 20, the oxygen coverage achieved on a Si(111)2×1 surface is by ~40% less than that achieved on a Si(111)7×7 surface under the same experimental conditions. By analogy, on the basis of the present results for the oxygen adsorption kinetics,

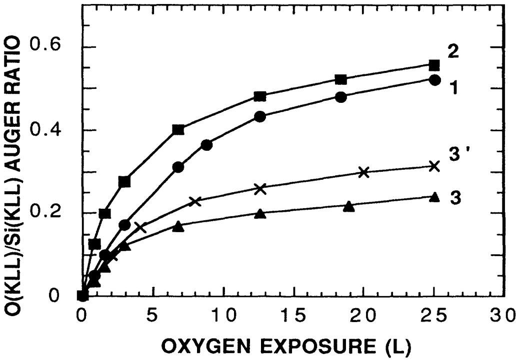

FIG. 3. Oxygen uptake curves for oxygen adsorption on 1, a clean Si(111)7×7 surface; 2, a 0.1 Na/Si(111)7×7 surface; 3, a "perfect" 0.1Na/Si(111)3×1 surface; 3′, an "imperfect" 0.1 Na/Si(111)3×1 surface. $T_a=300$ K.

we can suggest that the Na-induced (7×7)-to-(3×1) structural change causes reduction in the density of the surface dangling bonds. The exact mechanism of this reduction is not clear at the present stage. We can suggest the following two possible explanations: (i) the Na-induced (7×7)-to-(3×1) structural changes favor the formation Si—Si bridge surface bonds (dimerization of some neighboring Si atoms) which reduces the number of the active dangling bonds characteristic of the initial (7×7) structure or (ii) the bonding configuration of the Na adspecies, generating and stabilizing the 3×1 surface order, differs from the usual alkali adsorption bonding configuration (when the original Si surface structure is not affected) which leads to a drastic modification of the chemical bonds on the Si surface.

In summary, we have found that Na deposition on Si(111)7×7 at elevated temperatures produces a (3×1) reconstruction of the surface which offers more favorable adsorption states for Na. A characteristic difference between the Na/Si(111)7×7 and Na/Si(111)3×1 surfaces (covered with the same amount of Na) is the substantially reduced reactivity of the Na/Si(111)3×1 surface towards oxygen, which is indicative for considerable changes in the surface band structure.

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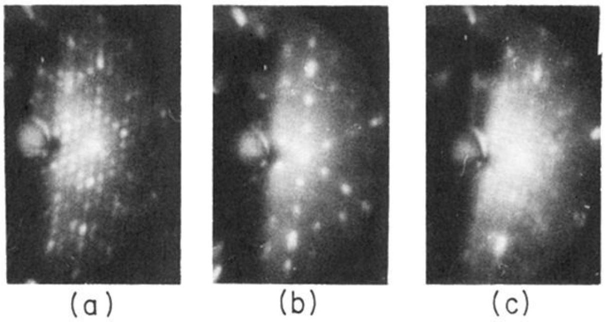

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