Electron-energy-loss spectroscopy study of the adsorption of aluminum on the silicon (111) 7×7 surface

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Electron-energy-loss spectroscopy and low-energy-electron diffraction have been used to study the adsorption of aluminum on the silicon (111) 7×7 surface at different substrate temperatures (T_s). It is shown that aluminum deposition at a T_s of 100–200°C results in the disappearance of the electronic-surface states of the silicon (111) 7×7 surface. New aluminum-induced loss peaks appear at 1.9, 3.2, 4.9, and 7.1 eV. It is further demonstrated that aggregation of aluminum atoms occurs on the silicon surface after the deposition of either two monolayers of aluminum at T_s = 100–200°C or one monolayer of aluminum at T_s = 600–700°C.

INTRODUCTION

Recently, electron-energy-loss spectroscopy (ELS) was used to study the changes of electronic surface states of different semiconductors when metal atoms are deposited onto semiconductor surfaces.[1] It was shown that gallium, a group-III metal, is capable of removing surface electronic states of silicon when one to two monolayers of gallium are deposited onto the silicon (111) 7×7 surface.[1] It would be interesting to see if aluminum, also a group-III metal, will behave similarly. Moreover, previous low-energy-electron-diffraction (LEED) studies showed that aluminum gives rise to different surface structures when deposited onto the silicon (111) 7×7 surface, depending on the surface concentration of aluminum atoms and the silicon surface temperature.[2,3] These surface structures are likely to produce different electronic surface states so that the surface states of the silicon-aluminum system will likely be a function of the metal-atom concentration on the silicon surface and the substrate temperature.

In this study, we used LEED and ELS to examine the surface structures and electronic transitions of the silicon-aluminum system. The energy-loss spectra involving both the silicon valence bands and the $2p$ core were obtained. The core-level loss spectra give information on the location of empty states above the Fermi level,[4] and complement the valence-band loss-spectra results, as shown later.

EXPERIMENTAL TECHNIQUES

The experiment was performed inside an ion-pumped stainless-steel vacuum system capable of a base pressure of less than 1×10^{-9} Torr. The system is equipped with LEED electron optics, an ion bombardment gun, and a quadrupole mass spectrometer. A double-pass PHI 15-25G cylindrical mirror analyzer with a coaxial electron gun was used for Auger analysis and ELS. The silicon crystal was positioned in front of the analyzer with the primary electron beam at normal incidence. The backscattered electrons were analyzed at $\theta = 42°$ over all azimuths. In taking ELS spectra involving the silicon valence bands, the incident electron energy was ~100 eV while in observing core excitations it was increased to ~150 eV. In both cases, the analyzer was operated in the retard mode corresponding to a constant energy resolution of 0.6 eV. The spectral features were enhanced by taking the second derivative $-d^2N/dE^2$ of the electron energy distribution.

The specimen used throughout the experiment was a 2500-Ω cm p-type silicon single crystal, oriented in the [111] direction, cut and polished. It was then etched in HF or HNO_3 solution to remove gross surface contaminants and rinsed in ethanol before being introduced into the vacuum system. In order to produce a clean silicon (111) surface with the 7×7 structure, the crystal was cleaned by argon-ion sputtering and then annealed at 800°C for about 30 min.

Aluminum was evaporated onto the silicon crystal surface from a tungsten spiral filament. A stainless-steel shutter, placed in front of the evaporator and operated by a rotary feedthrough, was used to control the aluminum deposition. Auger signals from the deposited aluminum layer and the silicon substrate could be monitored during evaporation. The average aluminum coverage was estimated from the attenuation of the silicon Auger peak at 91 eV,[5] assuming an electron mean free path of 6 Å.[6]

EXPERIMENTAL RESULTS

Effects of aluminum deposition at $100 < T_s < 200$ °C

In agreement with Lander and Morrison,[1] our LEED observations showed that the pattern cor-

responding to the silicon (111) 7×7 surface structure is preserved in the coverage range $0<\theta<0.5$, and that for aluminum coverages greater than 0.5, the one-seventh-order spots begin to disappear.

The energy-loss spectra of the silicon (111) 7×7 surface with various aluminum coverages are shown in Fig. 1. On the clean surface, the peaks labeled E_1 and E_2 are attributed to bulk interband transitions, whereas $\hbar\omega_p$ and $\hbar\omega_s$ are due to the silicon bulk and surface plasmons, respectively. S_1 is due to transitions from the occupied dangling-bond states and S_2, S_3 from back-bonding states.[7] After depositing 0.75 monolayer of aluminum onto the silicon surface, S_3 disappears while S_2 becomes weaker. S_1 seems to shift from 1.7 to 1.9 eV. The E_1 and E_2 transition energies increase slightly whereas the bulk plasmon energy decreases from 17.2 to 16.9 eV. At $\theta=1$, the bulk plasmon shifts further to 16.4 eV and the 1.9-eV transition remains strong.

In order to better understand the above trend of behavior, the corresponding energy-loss spectra due to the silicon 2p core-level excitation were taken and shown in Fig. 2, for $\theta=0$ [the clean silicon (111) 7×7 surface] and $\theta=1$. For the clean 7×7 surface, the core-excitation loss spectrum is similar to that of the silicon (100) 2×1 surface.[8] The 99.0-eV peak is due to the empty dangling-bond state, 99.8 eV being an exciton level and 100.7 eV being a peak in the silicon-bulk conduction-band density of states.[8] At $\theta=1$, the empty dangling-bond state disappears and the bulk conduction-band peak shifts to 100.5 eV.

Upon further deposition of aluminum up to $\theta=2$ at $100<T_s<200$ °C, the energy-loss spectrum (Fig. 3) shows strong loss peaks corresponding to the aluminum bulk and surface plasma excitations (15.2 and 10.4 eV, respectively). The 1.9-eV transition is also strong at this coverage. Increased deposition of aluminum results in the attenuation of the 1.9-eV peak, the appearance of the 2.5-eV transition, and the further growth of the

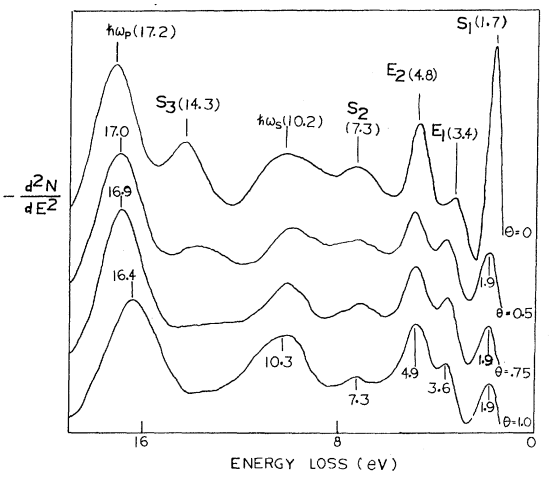

FIG. 1. Electron-energy-loss spectra of the silicon (111) (7×7) surface for various aluminum coverages, the latter being deposited at substrates temperatures between 100 and 200 °C.

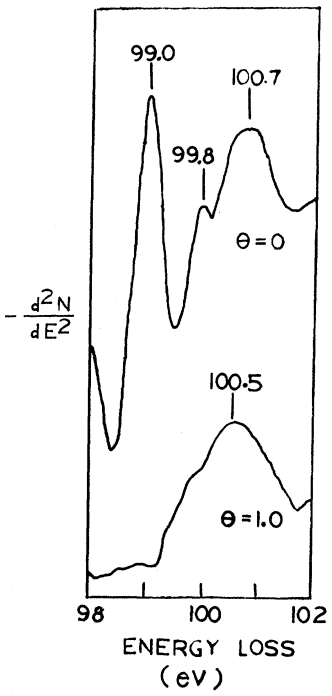

FIG. 2. Electron-energy-loss spectra due to the silicon 2p core excitation from the clean silicon (111) 7×7 surface ($\theta=0$ curve) and the same surface with one-monolayer aluminum deposited at a substrate temperature of 150 °C ($\theta=1$ curve).

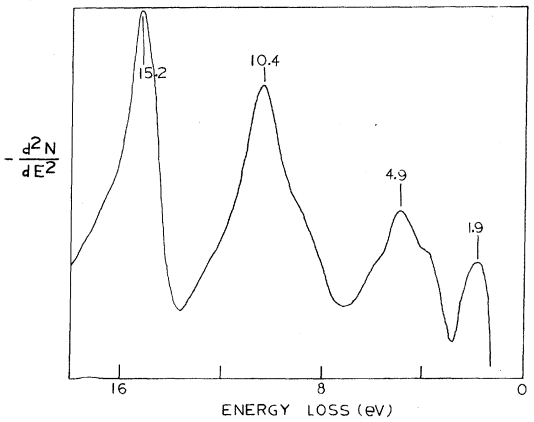

FIG. 3. Energy-loss spectrum of the silicon (111) 7×7 surface covered by two monolayers of aluminum deposited at a substrate temperature of 100–200 °C.

aluminum bulk and surface plasmon loss peaks (Fig. 4).

Effects of annealing the silicon (111) 7 × 7 surface with one monolayer of aluminum deposited at $100 < T_s < 200$ °C

After annealing at 600 °C for 30 min, the LEED pattern shows a set of hazy hexagonal reflections around each integral spot and weak one-seventh spots (Fig. 5). The energy-loss spectra arising from the valence bands and the silicon $2p$ core are shown in Figs. 6(a) and 6(b). One observes well-developed peaks at 7.0 and 3.2 eV. The bulk and surface plasmon losses occur at 16.7 and 11.2 eV, respectively (cf. 16.4 and 10.3 eV before annealing). Furthermore, the 1.9-eV transition has disappeared. The core-excitation energy-loss spectrum shows a substantial shift of the conduction-band density-of-states maximum.

Effects of aluminum deposition at elevated substrate temperatures (600–700 °C)

This particular substrate temperature is chosen because aluminum then gives rise to a well-defined surface structure on the silicon surface. LEED shows a distinct set of hexagonal reflections around each normal spot (Fig. 7), similar to that obtained by annealing, as discussed in the previous section. The loss spectrum (Fig. 8) indicates strong aluminum bulk and surface plasmon losses at 15.1 and 10.3 eV, respectively. The shoulder at 2.5 eV can be attributed to an aluminum bulk transition.[9] Apart from these transitions, the other features of the loss spectrum are similar to those obtained by annealing the silicon (111) 7×7 surface with one monolayer of aluminum deposited at $100 < T_s < 200$ °C.

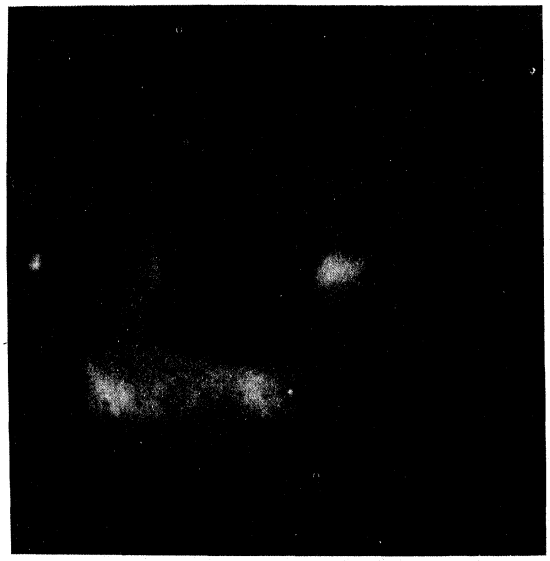

FIG. 5. LEED pattern obtained after annealing the silicon (111) 7×7 surface with one monolayer of aluminum deposited at $T_s = 100$–200 °C. The incident electron energy is 45 eV.

DISCUSSION

The deposition of one monolayer of aluminum onto the silicon surface at $100 < T_s < 200$ °C, removes the S_3 transition while S_2 becomes weaker. It is difficult to determine from Fig. 1 if the 1.9-eV peak is aluminum induced or a shifted S_1 transition. However, the corresponding core-excitation loss spectrum (Fig. 2) clearly shows the disap-

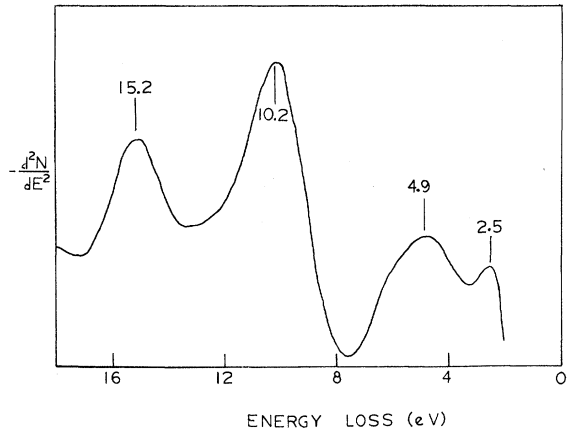

FIG. 4. Energy-loss spectrum of a 50-Å-thick aluminum layer deposited onto the silicon (111) 7×7 surface held at 150 °C.

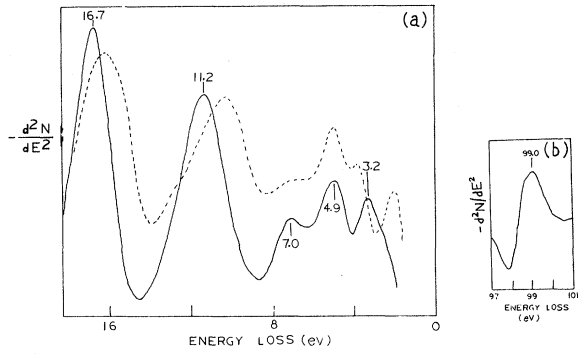

FIG. 6. (a) Energy-loss spectra of the silicon (111) 7×7 surface with one monolayer of aluminum deposited at $T_s = 100$–200 °C before (dotted curve) and after annealing at 600 °C for 30 min (solid curve). (b) The corresponding loss spectrum due to silicon $2p$ core excitation after annealing.

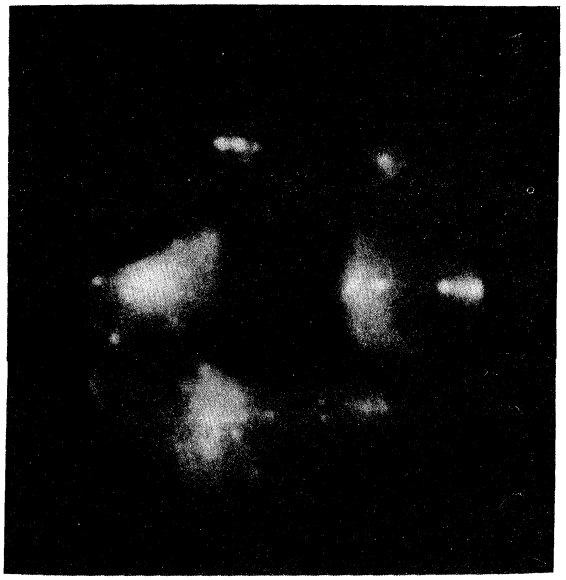

FIG. 7. LEED pattern from the silicon (111) 7×7 surface with one monolayer of aluminum deposited at 600–700 °C. The primary electron energy is 45 eV.

pearance of the dangling-bond state. Therefore, the S_1 state is indeed removed and the 1.9 eV peak can be assigned as an aluminum-induced transition. Moreover, the silicon bulk transitions (E_1 and E_2) shift slightly in energy indicating that the "bulk" band structure in the top few layers of the silicon lattice is affected by the presence of aluminum on the surface. In addition, there is a substantial decrease in the energy of the silicon bulk plasmon with increasing aluminum coverage. At $\theta = 1$, the bulk plasmon energy is 16.4 eV, which is between that of silicon (17.2 eV) and aluminum (15.3 eV). This suggests a possible interdiffusion of silicon and aluminum, which also explains the slight shifts of the silicon bulk transitions.

On annealing, the core-excitation loss spectrum

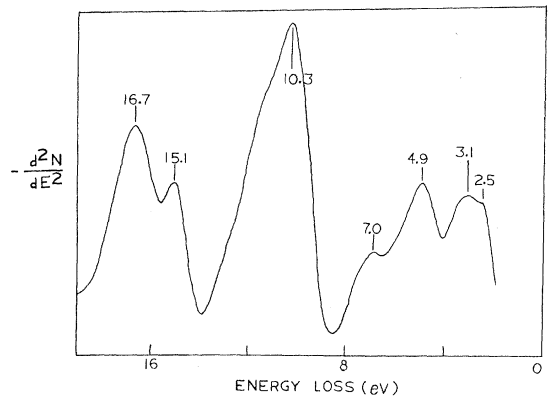

FIG. 8. Energy-loss spectrum of the silicon (111) 7×7 surface with one-monolayer aluminum deposited at 600–700 °C.

[Fig. 6(b)] shows a large shift in the position of the conduction-band density-of-states maximum as a result of annealing, so that the transitions at 3.2, 4.9, and 7.3 eV are probably due to the presence of aluminum on the silicon surface as well. These assignments also explain the apparent incomplete removal of the S_2 transition which overlaps with the 7.1-eV peak.

The appearance of strong aluminum bulk and surface plasmons after the deposition of (i) two monolayers of aluminum onto the silicon (111) 7×7 surface at 100–200 °C or (ii) one monolayer of aluminum onto silicon (111) 7×7 surface at 600–700 °C is most interesting. Because of the collective nature of plasma excitations, one would not expect to see these loss peaks from a thin (≤2 monolayers) uniform aluminum layer. Therefore, in both cases, aggregation of aluminum must have occurred. This can be understood as follows: in the initial stage of aluminum deposition in case (i), the aluminum atoms are sitting at preferred sites on the silicon (111) 7×7 surface, as evidenced by LEED. When all these sites are filled, arriving aluminum atoms will occupy random positions on the silicon surface. Further increase in coverage results in a significant probability of forming clusters with two or more aluminum atoms. There is strong evidence in the study of metal clusters that there exists a critical cluster size (approximately several atoms) above which cluster growth is favorable.[10] Formation of sufficiently large clusters gives rise to the observed plasmon loss peaks. On the other hand, at higher substrate temperatures (≳600 °C), the aluminum atoms have high surface mobilities, thereby resulting in a greater chance of forming critical size clusters even when the total number of aluminum atoms is smaller than the first case.

It may be noted that annealing a silicon surface with one monolayer of aluminum does *not* produce aluminum bulk or surface plasmon loss peaks. LEED observations indicate that the initial 0.5 monolayer of aluminum atoms are occupying certain preferred sites on the silicon surface. One would expect the aluminum atoms to be more tightly bound in these positions so that they are not mobile enough to participate in the clustering process.

CONCLUSION

We have used ELS and LEED to study the adsorption of aluminum on the silicon (111) 7×7 surface at different substrate temperatures. At substrate temperatures between 100 and 200 °C, aluminum deposition results in the removal of the silicon electronic surface states and at the same time,

gives rise to new states at 1.9, 3.2, 4.9, and 7.1 eV. There are also changes in the energy positions of the silicon bulk plasmon and bulk transitions. We attribute this to the interdiffusion of silicon and aluminum near the surface. On the other hand, our LEED observations show that the pattern corresponding to the silicon (111) 7×7 surface structure is preserved up to an aluminum coverage of one-half a monolayer. Further increase in aluminum coverage results in the disappearance of nonintegral spots. When the aluminum deposition takes place at a higher substrate temperature (600–700°C), a well-defined surface structure (Fig. 7) is obtained at one-monolayer aluminum coverage. Strong aluminum bulk and surface plasmon loss peaks in the corresponding energy-loss spectrum indicate the aggregation of aluminum atoms. The same phenomenon of aggregation also occurs for substrate temperatures between 100 and 200°C and an average aluminum coverage of two monolayers.

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FIG. 5. LEED pattern obtained after annealing the silicon (111) 7×7 surface with one monolayer of aluminum deposited at T_s = 100–200 °C. The incident electron energy is 45 eV.

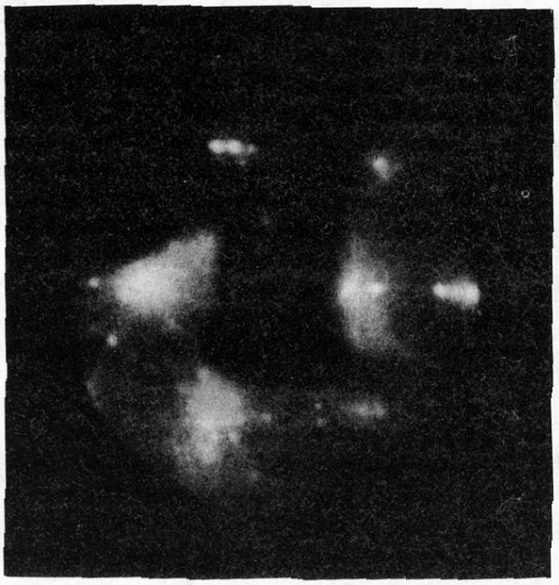

FIG. 7. LEED pattern from the silicon (111) 7×7 surface with one monolayer of aluminum deposited at 600–700 °C. The primary electron energy is 45 eV.