Secondary Ion Emission from Alkali/Si Systems

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Secondary ion yield and the work function change of Na, K and Cs on Si(100) and Si(111) were measured to discuss the details of secondary ion emission process. For the Si(100) surface, the secondary ion emission process was explained in terms of the electron tunneling model. On the other hand, it is difficult to apply the simple electron tunneling model to the experimental results for the Si(111) surface. It is suggested that the local electronic environment around the adsorbates might be taken into consideration.

1.Introduction

Secondary ion mass spectrometry (SIMS) is one of the most valuable techniques for analyzing materials using very high sensitivity (in general, from ppm to ppb level). The secondary ion yield, however, depends on several environmental and instrumental factors. For example, the relative positive or negative secondary ion yield under O^- or Cs^+ bombardment drastically changes for the detected species[1]. The ionization processes of secondary ion have not been fully understood so far. Therefore, the quantitative analysis is not easy in SIMS without the standard samples because of the complicated ionization processes of secondary ion. Thus, many ionization mechanisms have been proposed[2-8]. For example, the neutralization of secondary ion by electron tunneling is often used to explain the secondary ionization probability from Alkali covered metal surfaces[9]. In this model, the ionization probability is expressed as

$$P^+ \propto \exp[-(I-\Phi)/\varepsilon_0] \quad (I>\Phi) \quad (1)$$

where $\varepsilon_0 \propto v(z_c)\cos\theta$

where I is the ionization potential of secondary ion, Φ is the work function of metal[9]. ε_0 is the constant proportional to the normal component of the sputtered particle velocity from the metal surface. Z_c is the distance of the resonant charge transfer from the metal surface to the ion. Since the ionization of secondary ion takes place in the immediate vicinity of the surface (the distance between the sample surface and the ion is not more than about 1 nm), there exist some simple questions : Why does the secondary ion yield depend on the work function, which is the macroscopic quantity? Moreover, is the secondary ion emission processes explained by the microscopic information? In order to discuss the questions, we measured the work function change and the secondary ion intensity in detail for Alkali adsorbed Si(100) and (111) surfaces[11-13]. In the present paper, we will describe the experimental results and discuss the secondary ion emission processes from these systems.

2. Experimental

We studied the secondary ion emission processes through the use of the combined solid surface analysis equipment. The Auger electron spectrometry (AES) equipment was used to measure the growth mode of Alkali metal's thin film on Si surfaces, the saturation time of alkali adsorption and the monitoring of the contamination. The work function change measurement was performed by using the electron gun with the capability of irradiating perpendicular to the surface. SIMS equipment was used to investigate the secondary ion emission processes. In a UHV chamber, the base pressure was about 3.0×10^{-9} Pa, the working pressure during the deposition and the measurement of the work function change was better than 8.0×10^{-9}Pa. During the measurement of the secondary ion intensity, the pressure was 1.6×10^{-7}Pa because of using a differentially pumped ion gun. Specimens were B-doped p-type Si(100) and Si(111) surfaces. The specimen was cleaned by the direct resistive heating to about 1200℃. After cleaning, a sharp 2×1 and 7×7 RHEED pattern were observed for Si(100) and Si(111), respectively. Alkalis (Na,K and Cs) were deposited on the specimens at room temperature by using the commercial alkali dispensers (SAES getters). The coverage of Alkalis was monitored by Auger intensity. The Auger intensity of Alkalis increased linearly with the deposition time and then reached a constant value. On the other hand, the Auger intensity of Si decreased linearly and reached a constant value. Since the absolute coverage on the surface is not clear, we used the relative coverage(θ^*) which was defined as the relative

coverage(θ^*)=1 at the saturated points of Alkali and Si Auger intensity. The detailed work function change($\Delta\Phi$) measurement was performed by using the retarding potential method. The accelerating voltage of primary electron beam was 20V relative to the ground potential. We measured the threshold bias resulting from the scanning of the negative sample bias. The threshold bias changes with changing the work function, and we obtained $\Delta\Phi$ directly by the shift of the threshold bias. The secondary ion intensity was measured by the use of the quadrupole mass spectrometer. The energy of the secondary ions was not selected. Ar^+ beam was used as a primary beam, and the energy was 370eV. The current density was about 15-30nA/cm^2.

3. Results and Discussion

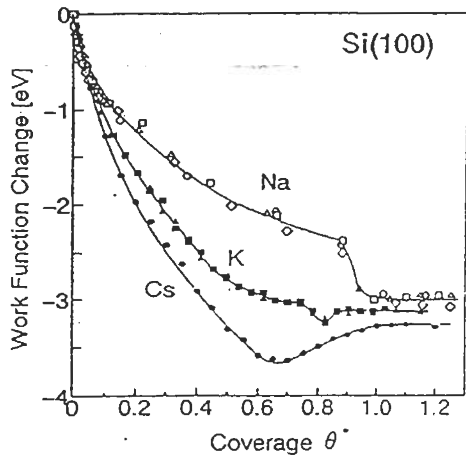

Fig.1. The Work Function Change ($\Delta\Phi$) vs. coverage θ^* for Alkalis/Si(100)

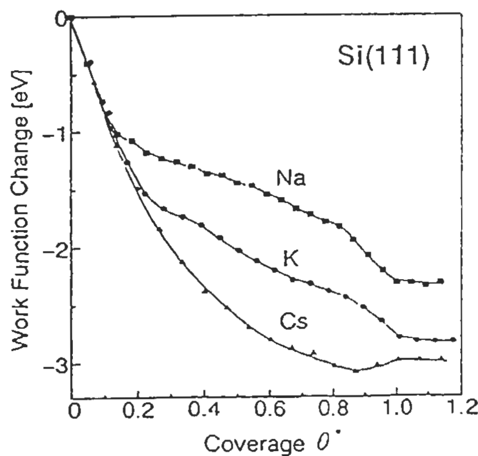

Fig.2. The work Function Change ($\Delta\Phi$) vs. coverage θ^* for Alkalis/Si(111)

Fig.1 shows the work function change ($\Delta\Phi$) vs. coverage θ^* for Alkalis/Si(100). On the Si(100) surface, the manner of $\Delta\Phi$ strongly depends on the Alkali species. At the initial stage, the work function decreases gradually for all Alkalis. However, the behavior is quite different from each other at high coverage. For Na/Si(100), the sudden fall is observed at around θ^*=0.9. For K/Si(100), the small dip is observed at around θ^*=0.8. And, for Cs/Si(100), the typical work function change resulting from the Alkali/metal surface is observed. Fig.2 shows the work function change ($\Delta\Phi$) vs. coverage θ^* for Alkalis/Si(111). On the contrary, the similar change is seen for Na and K/Si(111), except the absolute change. That is, the rapid decrease of the work function is followed by the gradual change. And the work function falls again at around θ^*=0.9. On the other hand, for Cs/Si(111), the behavior resembles to that for Cs/Si(100). The decrease of the work function is generally explained by the dipole field induced by positive ionized Alkalis. The conventional picture of Alkali adsorption proposed by Gurney[14] is such that at low coverage an essentially ionic bond is formed due to substantial charge transfer, and depolarization on at high coverage eventually leads to metallic or covalent bonding. Therefore, as Alkali adsorption increases, dipole moment μ decreases. Thus, as coverage θ^* increases, the ratio of the work function change is small. Only using this simple concept, however, it is difficult to explain the observed behavior of the work function change for Alkali/Si systems. The clear explanation of the behavior can not be achieved at present.

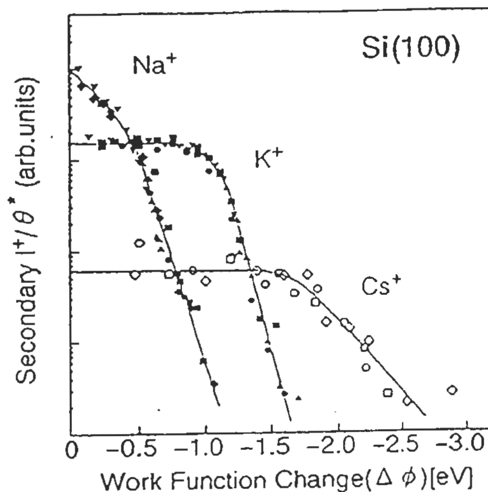

Fig.3. The dependence of the logarithm of the normalized intensity on $\Delta\Phi$ for Alkalis/Si(100)

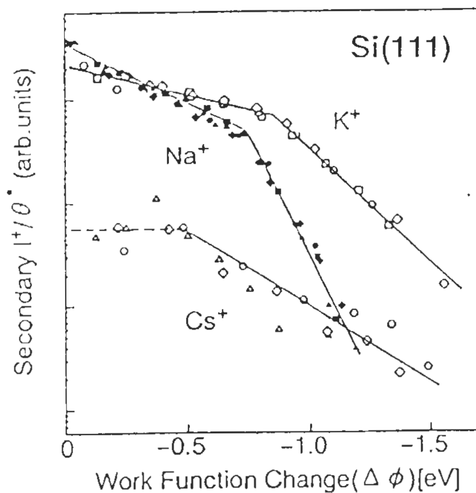

Fig.4. The dependence of the logarithm of the normalized intensity on ΔΦ for Alkalis/Si(111)

In order to discuss whether the electron tunneling model[9] can be used or not, the effect of the number of adsorbed atoms must be excluded. Then, we normalized the secondary ion intensity with the relative coverage θ^*, which is called the normalized intensity hereafter, and will discuss the dependence of normalized intensity on ΔΦ. Fig.3 shows the dependence of the logarithm of the normalized intensity on ΔΦ for Alkalis/Si(100). Several symbols correspond to the different experimental runs. For K and Cs/Si(100), the normalized intensities are nearly constant at small ΔΦ, and decrease exponentially about ΔΦ=-1.2eV for K and ΔΦ=-1.8eV for Cs. Between the constant value and the exponential decay regions, the gradual decrease of the normalized intensity can be observed. For Na/Si(100), the exponential decrease also can be seen above ΔΦ=-0.5eV, but the constant value is not observed. The normalized intensity gradually decreases from the initial stage of deposition in this case. The resonant tunneling is permitted when the ionization level coincides with E_F in the case of metals for the electron tunneling model[9]. For the semiconductor, the top of the valence band should be used instead of E_F. Thus, ΔΦ required to satisfy this condition is about -0.1, -0.9 and -1.4eV for Na, K and Cs/Si(100), respectively. Therefore, the exponential relationship between the normalized intensity and ΔΦ can be explained by the electron tunneling model[9]. The reason is when Φ is only slightly smaller than ionization potential(I), the crossing point(z_c) is too far away from surface for electron tunneling to be effective in the neutralization. In order to take place the effective neutralization, the more reduction of the work function is required. The gradual decrease of the normalized intensity before the exponential decay might be explained by the electron tunneling from the surface state around E_F. In fact, the normal-emission ARUPS spectra of the K/Si(100) surface as a function of the change in work function ΔΦ have been observed[15]. For -1.1eV≦ΔΦ, a peak at the E_F which is characteristic of a metallic sample is dominant; it shows a maximum intensity around ΔΦ=-0.7eV. For the clean Si(100) surface, a similar but weak metallic peak is found and is attribute to dangling bond states of Si dimers in area of disordered asymmetric dimers[16]. By the adsorption of Alkali atoms at the beginning, electron occupancy of these metallic states appears to be increased drastically. This surface electron state might have an effect on the electron tunneling from sample surface to ion. With these consideration, we can explain the above-mentioned phenomenon. Fig.4 shows the dependence of the normalized intensity on ΔΦ for Na, K and Cs/Si(111). For Na and K/Si(111), two exponential decays are observed. On the other hand, for Cs/Si(111), the starting point (ΔΦ value) of exponential decay is not fitted to ΔΦ<-1.5eV required for the neutralization of the secondary ion. Therefore, these experimental results can not be explained by simple electron tunneling model[9] related to the work function as the averaged electronic potential. Especially, for K/Si(111), the electron tunneling is permitted at ΔΦ≦-0.9eV. In the experimental observation, however, the normalized intensity decreases before -0.9eV. Such a different effect between Si(100) surface and Si(111) surface is predicted as being mentioned later. For Alkalis/Si(100), alkali adsorption appears to stabilize the buckled dimerization by adsorbing on the protruding Si side of the dimers[17]. Under the influence of buckling stabilization, thus, the Alkalis/Si(100) surface energy decreases. But, since Si(111) surface is very rigid structure, we may consider that the decrease of surface energy is due to the change of local electrostatic potential around adsorbates by Alkali adsorption. Recently, indeed, the neutralization of scattered ions concerning with the local electrostatic potential has been reported[18-22]. For Alkalis/Si(111), however, it is not clear whether the idea including the effect of the local electrostatic potential might

correct or not. Therefore, we expect the further discussions must be done in the future.

4. Conclusion

Alkali secondary ion emission process from Alkali/Si systems was discussed. In order to investigate the electron tunneling model[9], the work function change by Alkali metal adsorption was measured in detail. And, the relationship between the Alkali secondary ion yield and the work function change was discussed. For the Alkali/Si(100) systems, the Alkali secondary ion emission process was explained by the use of the electron tunneling model[9]. On the other hand, it is difficult to apply the simple electron tunneling model to experimental results for the Alkali/Si(111) systems. This indicates that the local electrostatic potential may be considered to explain the experimental results.

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