Kinetics of surface atoms during phase transition of Sc–O/W(100) system at high temperature studied by Auger electron spectroscopy

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ABSTRACT

The kinetics of surface atoms during the phase transition of a Sc–O/W(100) system at high temperature was investigated by Auger electron spectroscopy (AES). The simulation of the surface coverage was also performed by modeling the kinetics of surface phenomena, i.e., the oxidation, oxygen desorption, diffusion and surface segregation of Sc–O complexes, during phase transition. The results revealed that the stoichiometry of Sc–O complexes on the (1×1)-Sc–O/W(100) surface, the work function of which is low, is close to ScO, and its coverage is approximately 0.6. These findings suggest that the work function of the (1×1) surface is decreased by the formation of Sc–O electric dipoles. The increase in the work function during the transition from the (1×1) surface to the (2×1)-(1×2)-Sc–O/W(100) surface is due to the diffusion of Sc–O complexes into bulk W(100) and oxygen adsorption on the W(100) surface. By heating the (2×1)-(1×2) surface at 1700 K in an ultrahigh vacuum, Sc–O complexes segregate to the surface and excess oxygen adsorbing on the W(100) surface desorbs, resulting in the formation of the (1×1) surface. The present results confirmed that the work function of the Sc–O/W(100) system strongly correlates with the coverage of ScO on the surface, and the present kinetics models is effective for furthering investigation of the kinetics of surface atoms during the phase transition.

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1. Introduction

A Sc–O/W(100) emitter has been attracting attention as an alternative to the Zr–O/W(100) emitter widely used as an electron source for electron microscopes [1–3]. One of the excellent electron emission characteristics of the Sc–O/W(100) emitter is that the energy width of emitted electrons is almost half that of the Zr–O/W(100) emitter with the same degrees of brightness and stability. However, the low reproducibility of the electron emission properties restricts its practical use [2,3]. Therefore, a comprehensive understanding of the mechanism behind its electron emission properties is essential.

From a point of view of surface physics, the electron emission properties of the Sc–O/W(100) emitter is considered to be predominated by various surface phenomena such as oxidation, oxygen desorption, diffusion, and surface segregation occurring near the surface region of the Sc–O/W(100) system at 1500 K corresponding to the operating temperature of the emitter. This means that the improvement in the reproducibility of the electron emission properties can be achieved under limited preparation and operating conditions of the Sc–O/W(100) emitter. Therefore, it is necessary to understand such surface phenomena occurring at

high temperature of 1500–1700 K, the operating temperature of the Sc–O/W(100) emitter, in order to realize the practical use of the Sc–O/W(100) emitter by determining the optimum preparation and operating conditions.

In this regard, the authors have been involved in the surface characterization of the Sc–O/W(100) system using Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and work function measurement at high temperature [4–13]. Previous studies [4–13] have revealed that the Sc–O/W(100) surface has two phases with surface atomic arrangements of the (1×1) and (2×1)-(1×2) structures at high temperature. The (2×1)-(1×2)-Sc–O/W(100) surface is formed by heating at 1500 K in oxygen atmosphere. The work function of the (2×1)-(1×2) surface is high, which is close to that of a clean W(100) surface. The concentration of Sc on the (2×1)-(1×2)-Sc–O/W(100) surface is significantly low. In contrast to the (2×1)-(1×2)-Sc–O/W(100) surface, the (1×1)-Sc–O/W(100) surface is formed by heating at 1700 K in ultrahigh vacuum (UHV). The (1×1) surface has a low work function, which is lower than that of a clean W(100) surface by ~1.5 eV, and a high concentration of Sc. In addition, it has been confirmed that the reversible phase transition between the (1×1) and (2×1)-(1×2) surfaces occurs at high temperature of 1500–1700 K [11]. These findings have revealed that the preparation conditions for the Sc–O/W(100) surface and the oxygen partial pressure around the Sc–O/W(100) tip during

the operation at 1500 K are most important factors for the optimization of the preparation and operating conditions for the practical use of the Sc–O/W(100) emitter.

For realizing the practical use of the Sc–O/W(100) emitter, further understanding of the kinetics of surface atoms such as oxidation, reduction, diffusion and surface segregation, occurring at high temperature of 1500–1700 K is essential. In the present study, therefore, we aimed at the investigation of the kinetics of surface atoms during the phase transition by the detailed analysis of the AES spectral shape and intensity. The chemical bonding state of Sc atoms and the stoichiometry of Sc–O complexes were discussed on the basis of results of spectral shape analysis. Information on the coverage of Sc–O complexes was also deduced from the peak intensity. The kinetics of surface atoms, i.e., the oxidation, reduction, diffusion and surface segregation of Sc–O complexes, during phase transition was modeled, and the coverage and AES peak intensity of each species were simulated.

2. Experimental

All experiments were performed using a scanning Auger microscope (SAM-545, Physical Electronics Industries). The apparatus was equipped with a coaxial cylindrical mirror analyzer, a commercial LEED system (ELD-1000RV, EIKO), an ion gun for sputter cleaning, a Sc evaporator and a sample holder with a heater. The sample was a W(100) disk of 6.5 mm diameter with 1 mm thickness. The sample can be heated to ~1900 K required for flashing the W(100) disk by electron bombardment using a W filament located behind the W(100) disk. The present apparatus enables AES to be performed at a high temperature of ~1700 K [10]. LEED observation and work function measurement can also be performed at 1500 K [10]. The base pressure was ~5×10^{-9} Pa. Details of the experimental setup are described elsewhere [10].

The oxygen gas of 6 N required for the oxygen exposure was introduced into the chamber through a variable leak valve. The amount of deposited Sc was controlled by adjusting deposition rate, which was confirmed by AES, as described in Section 3.1. AES was performed using defocused 5 keV electrons of 50–100 nA in the scanning mode to prevent the surface segregation of Sc atoms induced by electron irradiation at high temperature [13,14]. The beam diameter, which was determined as 2σ of the Gaussian profile, where σ is the standard deviation, was ~0.35 mm, the scanning area was 0.28×0.24 mm^2, and the scanning rate was 30 s^{-1}. It was confirmed that the electron-induced surface segregation of Sc at high temperature can be completely avoided by irradiation of primary electrons under these conditions [13]. Work function was measured at room temperature (RT) by the secondary-electron method [15–19]. In the secondary-electron method, work function is measured as a value relative to that of the reference, $\Delta\Phi$. $\Delta\Phi$ is obtained from the difference in the onset energy of secondary-electron spectra from the sample and reference surfaces, $E_{sample}-E_{ref}$, using $\Delta\Phi = (E_{sample}-E_{ref})/C_{corr}$, where C_{corr} is the correction factor required for the precise measurement [15–19]. In the present study, a clean W(100) surface was used as the reference for the work function measurement, and all the value of work function, $\Delta\Phi$, is shown as a value relative to that of the clean W(100) surface. LEED observation was performed using ~65 eV electrons of ~2 µA at RT. Details of the AES at high temperature are described elsewhere [13].

The procedures of the preparation of the (2×1)-(1×2)- and (1×1)-Sc–O/W(100) surfaces were the same as those in our previous studies [11–13]. A W(100) surface was cleaned by repeated sputterings using 500 eV Ar$^+$ ions of ~1 µA and flashing at 1900 K. The (2×1)-(1×2)-Sc–O/W(100) surface was prepared on the W(100) surface by depositing ~5 ML of Sc at 1500 K in oxygen

atmosphere of ~5×10^{-5} Pa. The transition from the (2×1)-(1×2) surface to the (1×1) surface was induced by heating at 1700 K in UHV below ~8×10^{-8} Pa. The phase transition from the (1×1) surface to the (2×1)-(1×2) surface was induced by exposure to oxygen of ~5×10^{-7} Pa at 1500 K. Details of AES during the phase transition [12,13] are described elsewhere.

To investigate the chemical bonding state of Sc atoms on the Sc–O/W(100) surface during the phase transition between the (1×1) and (2×1)-(1×2) surfaces, two reference surfaces were prepared [13]. One reference surface was a Sc thin film of 2.2 Å thickness deposited on a W(100) surface, the thickness of which was confirmed as described in Section 3.1. The other was an oxidized Sc film prepared by oxygen exposure to the above reference surface of the metallic Sc film at RT until oxidation saturated. Reference AES spectra were measured for both the metallic and oxidized Sc films.

3. Results and discussion

3.1. Measurement of deposition rate

To estimate the thickness of the deposited Sc film from the deposition rate of the present Sc evaporator, deposition rate was measured by quantitative AES. The intensity of the Sc-LMM peak of the Sc film deposited on the W(100) substrate, which is normalized by the W-NVV intensity from bulk W, $I_{Sc-LMM}^{Sc/W}$, is given by

$$I_{Sc-LMM}^{Sc/W} = \frac{I_{Sc-LMM}^{bulk\ Sc}}{I_{W-NVV}^{bulk\ W}} \frac{R_{Sc-LMM}^{W}}{R_{Sc-LMM}^{Sc}} \left[1 - \exp\left(-\frac{r_{Sc} t_{Sc}}{\lambda_{Sc-LMM}^{Sc} \cos\theta} \right) \right], \quad (1)$$

where $I_{Sc-LMM}^{bulk\ Sc}$ is the Sc-LMM intensity from bulk Sc, $I_{W-NVV}^{bulk\ W}$ is the W-NVV intensity from bulk W, r_{Sc} is the deposition rate, t_{Sc} is the deposition time, λ_{Sc-LMM}^{Sc} is the attenuation length of Sc-LMM Auger electrons in Sc, and $\theta = 42.3°$ is the detection angle of Auger electrons. R_{Sc-LMM}^{W} and R_{Sc-LMM}^{Sc} are the backscattering factors for Sc-LMM Auger electrons in W and Sc, respectively. $R_{Sc-LMM}^{W}/R_{Sc-LMM}^{Sc}$ describes the increase in the Sc-LMM peak intensity from the thin Sc film on the W(100) substrate compared with that from bulk Sc, which arises from the backscattering effect of the W(100) substrate. The W-NVV intensity from the W(100) substrate beneath the Sc thin film normalized by the W-NVV intensity from bulk W, $I_{W-NVV}^{Sc/W}$, is given by

$$I_{W-NVV}^{Sc/W} = \exp\left(-\frac{r_{Sc} t_{Sc}}{\lambda_{W-NVV}^{Sc} \cos\theta} \right), \quad (2)$$

where λ_{W-NVV}^{Sc} is the attenuation length of W-NVV Auger electrons in Sc.

Marks in Fig. 1 shows the variations in the peak-to-peak (p–p) intensities of the Sc-LMM and W-NVV peaks experimentally obtained for the Sc film on the W(100) substrate as functions of deposition time, t_{Sc}. The thick and thin solid lines, respectively, show the Sc-LMM and W-NVV peak intensities, $I_{Sc-LMM}^{Sc/W}$ and $I_{W-NVV}^{Sc/W}$, calculated using Eqs. (1) and (2). $R_{Sc-LMM}^{W}/R_{Sc-LMM}^{Sc}$ was 1.31 at a normal incidence [20,21], and $\lambda_{Sc-LMM}^{Sc} = 11.67$Å and $\lambda_{W-NVV}^{Sc} = 8.48$Å were calculated using the Seah–Dench empirical equation [22]. r_{Sc} was determined to be 0.90 Å/min by best-fitting Eqs. (1) and (2) to the experimental data, and the root mean square (RMS) difference between the experiment and the calculation was 0.090. A fairy good agreement is observed between the simulated and experimental results.

For comparison, Sc-LMM and W-NVV peak intensities were calculated without correction for the backscattering effect induced by the W(100) substrate, i.e., $R_{Sc-LMM}^{W}/R_{Sc-LMM}^{Sc} = 1.00$. The results of the bestfitting were plotted by the thick and thin dotted lines for Sc-LMM and W-NVV peak intensities, respectively. The RMS differ-