Cryogenic TOF-SIMS around sublimation temperature of quench condensed-noble gas (Ne, Ar, and Kr) films

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Abstract

A possible TOF-SIMS analysis of surface phase transitions has recently been proposed for limited cases such as polymers and ionic liquids. In the present study, we have extended this analysis to quench condensed noble gas films. The newly developed cryogenic TOF-SIMS allowed both measurements of TOF-SIMS below 4 K and low-energy ion scattering spectroscopy that is used to prepare a clean surface. It was found that the TOF-SIMS intensity variation by increasing the temperature at a constant ramp rate (temperature-programmed TOF-SIMS) shows steep changes due to sublimation. Thus, the possibility of analyzing the surface phase transition at the local region defined by the incident ion beam of (cryogenic) TOF-SIMS was demonstrated in the present study.

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I. INTRODUCTION

TOF-SIMS has established itself as a powerful technique for analyzing outermost surfaces. The surface sensitivity of TOF-SIMS is extreme, which is a critical feature for application in various scientific and technological fields where the outermost surface plays an important role. The application range of TOF-SIMS is expanding with the help of instrumental innovations, a deeper understanding of the ion-surface interaction, and accelerated processing for the measured data.

One of the advanced applications of TOF-SIMS may be the analysis of surface phase transitions. Recent studies have suggested that the surface phase transition is detected by measuring the TOF-SIMS intensity with increasing sample temperature. For example, Vinx et al. [1] and Poleunis et al. [2] have reported that the temperature dependence of TOF-SIMS signal intensity shows an inflection point related to the glass transition temperature of polymer surfaces. In addition, Souda has indicated that the TOF-SIMS signal intensity measured by increasing the sample temperature at a constant ramp rate (temperature-programmed TOF-SIMS) shows a steep change at the glass transition, crystallization and melting of the ionic liquid surface [3, 4]. Furthermore, Fu et al. have shown that the temperature dependence of the TOF-SIMS intensity signal shows a step change at the surface glass transition of polystyrene films [5, 6]. Our recent study on quench condensed - hydrogen films using cryogenic TOF-SIMS has also suggested that the solid-to-gas phase transition, that is the sublimation, is detected by the temperature-programmed TOF-SIMS measurement [7]. These studies suggest the possibility of a unique analysis of the structural phase transition of the local area on the outermost surface defined by the incident ion beam of TOF-SIMS. The phase transition analysis of the surface local region is obviously important not only for fundamental materials science, but also for various practical devices using surface and interface properties. However, to the best of our knowledge, the detection mechanism remains unclear. Therefore, it is not clear that this method of analyzing the surface phase transition by TOF-SIMS is applicable to materials other than polymers, ionic liquids, and hydrogen.

In our previous temperature-programmed TOF-SIMS study on the solidified hydrogen film, a steep change in the intensity was observed at the sublimation temperature [7]. Since the observed temperature for the intensity variation agrees with the desorption temperature of a hydrogen molecule from the solid surface, the possibility of the surface melting was proposed to be ruled out. The surface melting of solid hydrogen has attracted attention as the approach to realizing the superfluidity of hydrogen. [8, 9] Thus, the existence of the surface melting on solid hydrogen itself should be revealed, which was the motivation of our previous study. The surface melting has often been suggested at solid vapor interfaces that take place in prior to sublimation. It is crucial for understanding the fundamental process at surfaces, such as wetting, adsorption, and friction, and therefore, it has been widely studied both from experiments and theories [10–15].

In the present study, we extended the application of our cryogenic TOF-SIMS to quench condensed-noble gas (Ne, Ar, and Kr) films. In the present paper, it will be described that the solid-to-gas phase transition, that is sublimation, of the solidified noble gas surfaces is analyzed by temperature-programmed TOF-SIMS, and therefore, it is useful for the analysis of surface phase transitions.

II. EXPERIMENTS

Experiments were performed in an ultra-high vacuum (UHV) analysis chamber (7×10^{-9} Pa) configured for home-built TOF-SIMS. The details of the experimental setup have been described elsewhere [7]. Briefly, a 2 keV He^+ ion beam is used for the primary ion of the TOF-SIMS measurement, which was pulsed by the pulsed electric field with a pulse width of 500 ns and a duty ratio of 1.5%. The beam diameter at the sample position was approximately 2 mm. The secondary ions were detected by an electrostatic hemispherical energy analyzer (VSW, CL50), where the pass energy and the analysis energy of the analyzer were set to 90 eV and 10 eV, respectively. Thus, the secondary ions measured in TOF-SIMS have a kinetic energy of 10 eV, which was accelerated to 90 eV inside the energy analyzer. In our TOF-SIMS measurement, the beam fluence was less than 10^{12} ion·cm^{-2} which is the typical condition for static SIMS. The temperature-programmed TOF-SIMS was performed by raising the sample temperature at the constant rate of 2 K/min from the quench condensation temperature. The continuous He^+ ion beam was used for low-energy He^+ ion scattering spectroscopy (LEIS), which was needed to confirm the cleaning of the sample surface. Since TOF-SIMS and LEIS share the energy analyzer in our setup, the analysis point was identical between these techniques.

The substrate for quench-condensation of noble gases was tantalum foil of thickness 0.1 mm (purity: 99.95%, Nilaco, Japan). Before the quench condensation, the Ta substrate surface was cleaned by several cycles of flash heating to above 1800 K in UHV and 2 keV Ar^+ ion sputtering. The successful surface cleaning by the surface cleaning procedure was confirmed by LEIS.

We exposed the cleaned Ta substrate surface to noble gases (Ne, Ar, and Kr) below 4 K to prepare the quench-condensed solid film. The purity of the gases was more than 99.999% for Ne, 99.9999% for Ar, and 99.999% for Kr (Suzuki Shokan Co., Ltd). These gases were introduced into the UHV chamber via a variable leak valve. The exposure is expressed in the present paper by Langmuir (L), where 1 L = 1.33×10^{-4} Pa·s. The partial pressure of the introduced gas during the exposure was controlled to be 1.33×10^{-7} Pa for 0.1 L or less, 1.33×10^{-6} Pa for over 0.1 L to 2 L, 1.33×10^{-5} Pa for over 2 L to less than 25 L, and 1.33×10^{-4} Pa for over 25 L. The TOF-SIMS measurements were performed after recovery of the post-exposure vacuum below 1×10^{-6} Pa.

We used a GM refrigerator (Iwatani, HE05) together with a homemade sample stage and a radiation shield to construct a UHV-compatible cryostat that allowed sample cooling to below 4 K during TOF-SIMS measurement as well as the quench condensation of noble gases. The sample temperature was measured by a silicon diode sensor (Lake Shore, DT-670-SD-1.4H) placed near the sample.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature-programmed TOF-SIMS results on the quench condensed- Ne film. The Ne^+ intensity is plotted as a function of the increasing sample temperature for different exposures from 0.3 L to 1000 L. The features of the profile are summarized as follows. In the low exposure below 3 L, the Ne^+ signal vanishes at about 22 K (position (i)). The increase of the exposure to 10 L causes the appearance of a new structure at about 7 K (position (ii)). This new structure changes the shape of the profile with further increase of exposure: it shows a simple decrease of intensity with the increase of temperature at position (ii) below 100 L, while above 300 L, it consists of the opposite increase of intensity at position (ii) followed by the decrease of intensity at a higher temperature. Thus, the intensity variation above 300 L forms a peak starting at position (ii). It is noted that the onset temperatures at which the intensity change starts above 10 L are identical (position (ii)) between the different exposures.

The tendency of the temperature-programmed TOF-SIMS profile summarized above for Ne is quite similar to that observed for solidified hydrogen films in our previous study [7]. In the case of the hydrogen, the structure at position (i) was attributed to the desorption of adatoms directly contacting the substrate surface, while the structure at position (ii) was attributed to the sublimation from the quench-condensed film. The sublimation temperature of Ne reported for the pressure of $10^{-6} - 10^{-7}$ Pa under which the measurement was performed in the present study agrees with the temperature of position (ii) [16]; therefore, the structure at position (ii) is attributed to the sublimation. On the other hand, from the similarity to the hydrogen case, it is likely that the structure (i) is due to the elimination of the Ne adatoms from the Ta surface by desorption.

Figure 2 shows temperature-programmed TOF-SIMS profiles on the quench-condensed Ar film. The essential features of the profile are very similar to those observed for Ne, namely the signal disappearance at position (i) and the intensity variation starting at position (ii). The intensity variation at position (ii) is dependent on the exposure as similar to Ne: it simply decreases as the temperature at position (ii) in the initial stage while it oppositely increases and forms a peak at larger exposures. The temperature of position (ii) again agrees with the reported sublimation temperature for Ar [16].

Figure 3 shows temperature-programmed TOF-SIMS profiles on the quench-condensed Kr film. Again, the profile shows a similar trend to that observed for Ne. The temperature of position (ii) agrees with the reported sublimation temperature for Kr [16].

The full mass spectra are shown in Fig. S1 of supplementary, where the $Ne^+/Ar^+/Kr^+$

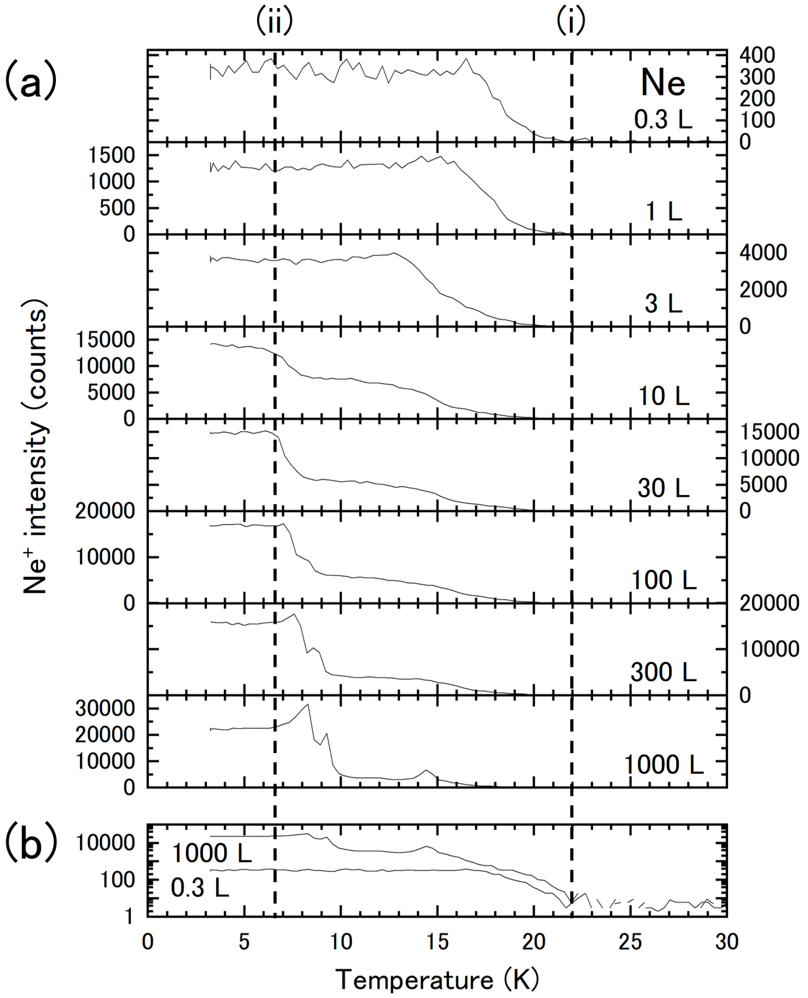

FIG. 1: Temperature-programmed TOF-SIMS profiles of the Ne^+ ion measured on the Ne film quench condensed on the Ta substrate. The Ne film was grown by exposing the Ne gas to the Ta substrate below 4 K, which was immediately followed by the temperature-programmed TOF-SIMS measurement performed by increasing the sample temperature at a constant rate of 2 K/min. All profiles are shown in the linear scale in (a) and the selected profiles (0.3 L and 1000 L) are shown in the logarithmic scale in (b).

peaks are clearly observed. It has been reported in the paper by Wilson [17] that the SIMS relative sensitivity factors (RSF) of Ne, Ar and Kr are quite high; hence the ion yields of these noble gases are very low. The RSF reported by Wilson are for implanted standards prepared in Si, GaAs and diamond. Therefore, the reported RSF for Ne, Ar and Kr are for these noble gases implanted in Si, GaAs or diamond. The situation is different in the present study, where the ionization of the noble gases takes place on the solid film of the

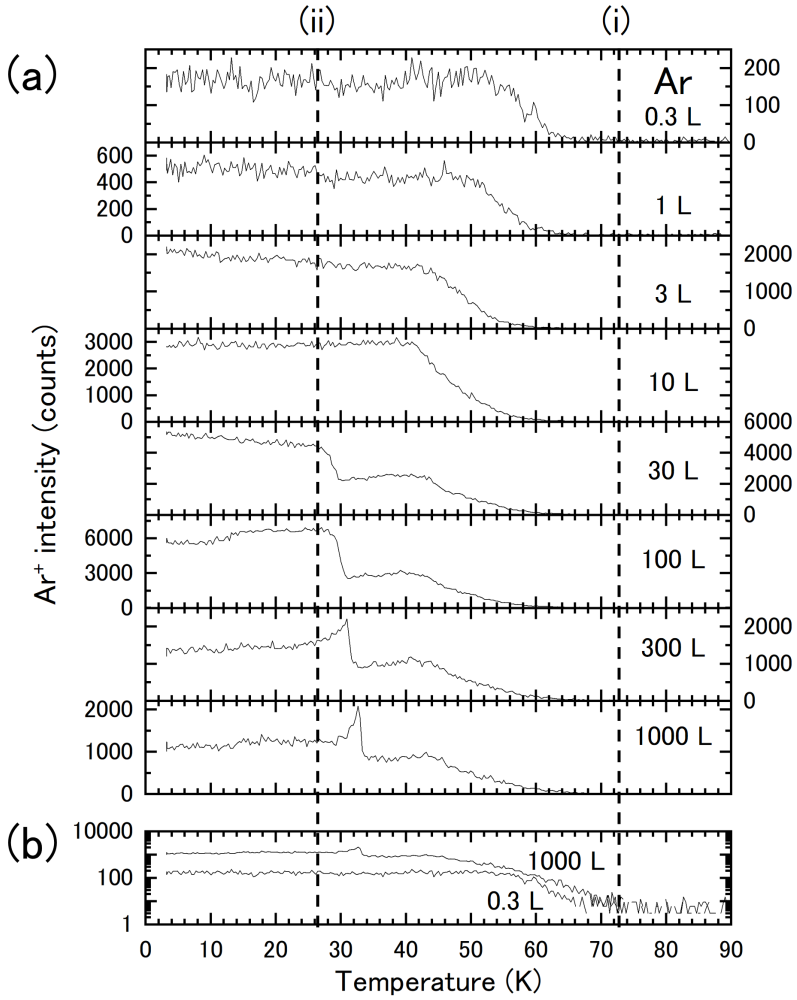

FIG. 2: Temperature-programmed TOF-SIMS profiles of the Ar$^+$ ion measured on the Ar film quench condensed on the Ta substrate. The Ar film was grown by exposing the Ar gas to the Ta substrate below 4 K, which was immediately followed by the temperature-programmed TOF-SIMS measurement performed by increasing the sample temperature at a constant rate of 2 K/min. All profiles are shown in the linear scale in (a) and the selected profiles (0.3 L and 1000 L) are shown in the logarithmic scale in (b).

noble gases themselves. It is believed that this difference, related to the matrix effect in the ionization mechanism, gives a large difference in the ionization yield of noble gases.

From the series of measurements shown in Figs. 1 to 3, it is concluded that there are two features in the temperature-programmed TOF-SIMS profiles on a quench-condensed noble gas film: the intensity decrease due to the desorption of noble gas adatoms from the surface

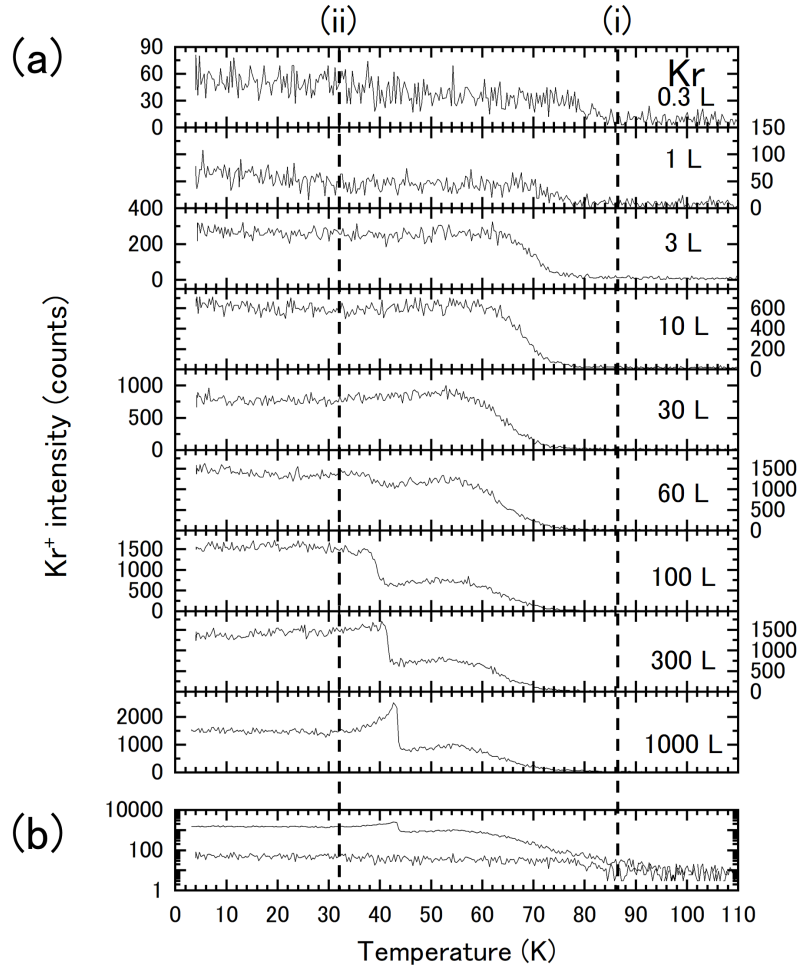

FIG. 3: Temperature-programmed TOF-SIMS profiles of the Kr$^+$ ion measured on the Kr film quench condensed on the Ta substrate. The Kr film was grown by exposing the Kr gas to the Ta substrate below 4 K, which was immediately followed by the temperature-programmed TOF-SIMS measurement performed by increasing the sample temperature at a constant rate of 2 K/min. All profiles are shown in the linear scale in (a) and the selected profiles (0.3 L and 1000 L) are shown in the logarithmic scale in (b).

at position (i) and the exposure-dependent intensity variation due to sublimation at position (ii). The temperature of position (i) is higher than that of position (ii). This is probably due to the smaller interatomic bond strength in the solidified noble gas film compared to the noble gas adatom-Ta surface bond.

Figure 4 shows the TOF-SIMS intensities of Ne$^+$, Ar$^+$, and Kr$^+$ in addition to that of the

Ta-derived monocation as a function of the exposure in measurements separate from those of Figs. 1 to 3. The Ta-derived +1 ions are a monocation of Ta bound to contaminant molecules still present on the surface after surface cleaning, such as hydrogen, water and hydrocarbons, in addition to Ta^+.

The intensity variations are similar between Ne^+, Ar^+, and Kr^+. They show a rapid increase in the initial stage of the exposure, which reaches the maximum below 100 L. Further increase of the exposure reduces the intensity of Ar^+, while the intensities of Ne^+ and Kr^+ remain almost the same. On the other hand, the intensity of the Ta-derived monocation increases steeply in the initial stage of the exposure. The exposure amount for the maximum of the Ta-derived monocation agrees with those for the maximum of Ne^+, Ar^+, and Kr^+. Further increase of the exposure drastically decreases the Ta-derived monocation intensity, which vanishes at very large exposures such as 1000 L.

It is observed that the Ta-derived monocation intensity is quite small on the clean surface, which increases with the exposure of Ne, Ar, and Kr. This indicates that the secondary ion emission of the Ta-derived monocation is enhanced by the adsorbed Ne, Ar, and Kr on the surface.

It is well-known that the adsorbed molecule by quench condensation forms the low-density sherbet-like structure because the molecule can not migrate on the surface at low temperatures. This sherbet-like film of the noble gas likely does not completely cover the Ta surface at the large exposure of 100 L because the Ta-derived monocation signal is detected at this exposure. The vanish of the Ta-derived monocation signal at larger exposure as 1000 L indicates that the Ta surface is fully covered by the solidified noble gas film with this exposure.

The TOF-SIMS intensity I is generally dependent on the surface density of the precursor ion C_j as

$$I = I_p S K_j \eta C_j, \tag{1}$$

where I_p the primary ion beam current, S the sputtering yield, K_j the ionization rate, and η the instrumental function. Assuming these parameters are constant except for C_j before and

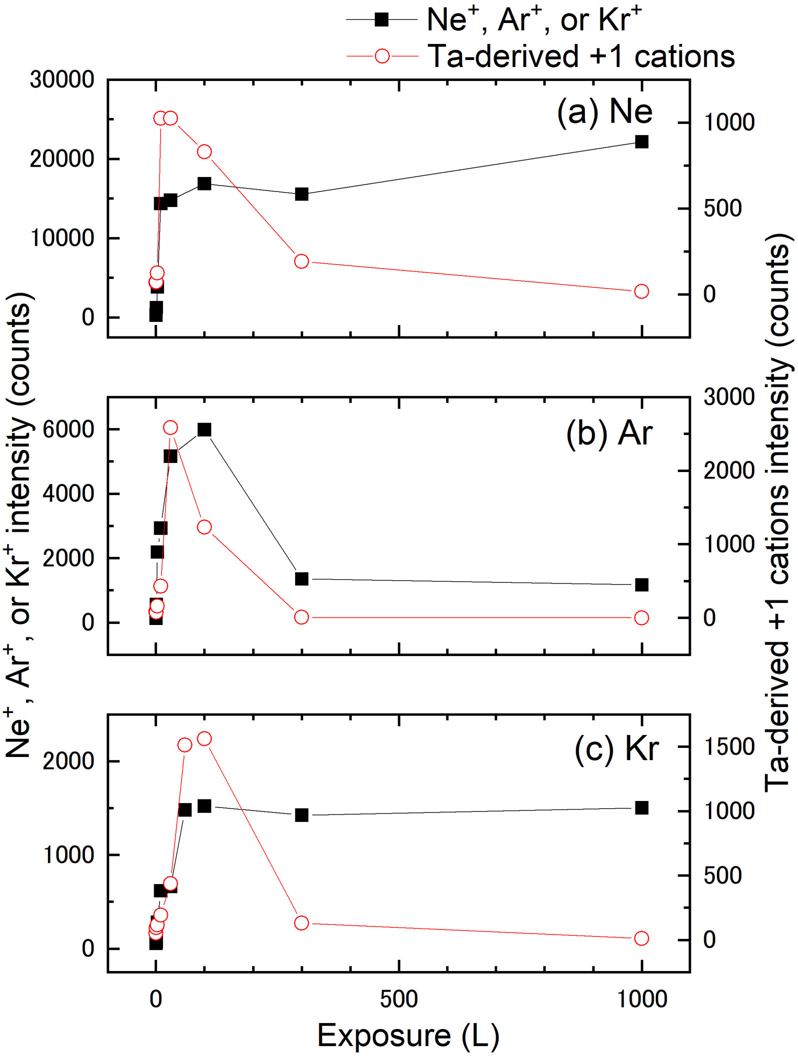

FIG. 4: (Color online) TOF-SIMS intensity of (a) Ne, (b) Ar, and (c) Kr (solid black squares) and Ta-derived cations (open red circles) as a function of exposure below 4 K. The data are obtained from those shown in Figs. 1, 2, and 3 at 4 K.

after the structural phase transition, the TOF-SIMS intensity changes at a phase transition that is normally accompanied by the change of density.

The noble gas atoms are stuck at the first position they reach on the surface, which is the mechanism of low-density film formation. It is noted that re-adsorption of the sublimated molecules smooths the rough surface, hence the density of the film increases. [7] Therefore, the quench-condensed molecular film is densified at the sublimation temperature while the total number of molecules in the film decreases due to desorption. We consider that this is the mechanism for the appearance of the peak at position (ii). In other word, the intensity variation observed at position (ii) is considered as a result of two competing effects: the increase of the film density and the decrease of the surface coverage.

As stated in the experimental section, all TOF-SIMS measurements were performed after recovery of the post-exposure vacuum below 1×10^{-6} Pa. Thus, the initial vacuum conditions were almost the same between the TOF-SIMS measurement with different exposures. However, during the temperature programmed measurements, the partial pressure of the noble gas varied due to the desorption from the sample surface and evacuation by the vacuum pump. Since the amount of the noble gas adsorbing on the surface depends on the exposure, the vacuum behavior during the temperature programmed measurements differed between different exposures. Therefore, the balance between the desorption and the re-adsorption of the noble gas atom which is the mechanism of the TOF-SIMS intensity variation at position (ii) in Figs. 1, 2, and 3 depends on the exposure. This may be related to the exposure dependent profile shape of the temperature programmed TOF-SIMS at position (ii).

It is observed in Figs. 1, 2, and 3 that the temperature at which the TOF-SIMS intensity starts to decrease shifts to the low temperature side with increasing the exposure in the range of 0.3-3 L. As mentioned above, the TOF-SIMS intensity above the sublimation temperature is considered to be determined by two competing effects: the densification of the film and the decrease of the surface coverage. Thus, the flat profile of the temperature-programmed measurement suggests that these two effects are balanced. The decrease of the intensity is attributed to the imbalance between these two effects, indicating that the decrease of the surface coverage is the primary factor affecting the profile shape. Since the average thickness of the noble gas film decreases with decreasing the exposure, the temperature at which the imbalance begins shifts to lower temperatures with decreasing the exposure.

Surface melting of solidified noble gases has been claimed experimentally by several groups, although we are not aware of recent studies on this topic. [15, 18–21] The surface melting has often been analyzed using powder samples to enhance the surface volume ratio, although the melting effect may be affected by the confinement effect [22]. Since the sublimation temperature observed in the present study is consistent with the desorption energy from the solid surface as reported by Ferreira et al [16], the possibility of the surface melting in prior to sublimation seems less likely.

IV. CONCLUSION

We applied cryogenic TOF-SIMS analysis to quench-condensed noble gas (Ne, Ar, and Kr) films grown on a polycrystalline Ta foil. The temperature-programmed TOF-SIMS profile was sensitive to the surface structure of the film, which was found to show two prominent features. One is due to the sublimation of the film and the other is due to the elimination of the noble gas adatom from the surface by the desorption. Therefore, it is suggested that (cryogenic) TOF-SIMS is useful for analyzing the surface solid-to-gas phase transition at the local point defined by the primary ion beam.

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