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Measurement of crystallization temperature of Pd-based amorphous alloy thin film by energy dispersive X-ray reflectometry

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X-ray reflectivity of a Pd-based amorphous alloy thin film was measured by an energy dispersive method in the vicinity of crystallization temperature upon heating. A large number of oscillations of X-ray reflectivity were clearly observed, because the surface of the amorphous alloy thin film is extraordinary smooth. The oscillations of X-ray reflection became smaller after crystallization of the film, as the surface roughness of the film is increased by grain boundaries. Thickness of the film estimated from the distance between the peaks of the oscillations was decreased when the film was heated to higher temperature than 140 °C. It is considered that the crystallization temperature of the Pd-based amorphous alloy thin film is about 140 °C.

Key words: amorphous alloy thin film, X-ray reflectivity, crystallization

1. INTRODUCTION

Amorphous alloys possess various attractive properties for structural materials, such as high strength, soft magneticity and corrosion resistance. Because of those excellent properties, amorphous alloy thin films are promising for micro/nano-electro mechanical systems (MEMS/NEMS). In order to use amorphous alloy thin films for MEMS/NEMS devices, measuring crystallization temperature (T_x) of the films is important. For amorphous thick films, whose thickness is larger than several micron-meter, it is able to measure T_x by using the conventional thermal analysis, e.g. differential scanning calorimetry (DSC) or thermal mechanical analysis (TMA), as same as bulky amorphous specimens. However, it is difficult to measure T_x by those thermal analytical methods for thin films. It is considered that measuring resistance of the film upon heating is one of the traditional methods to determine T_x of amorphous thin films. But electronic current flows only on the surface of the thin films, thus it is necessary to develop a new method to measure T_x of amorphous alloy thin films. In the present study, the thickness of a Pd-based amorphous alloy thin film was examined upon heating by means of energy dispersive X-ray reflectivity measurement.

2. EXPERIMENTAL PROCEDURES

Pd-based amorphous alloy ribbons were prepared by melt-spinning using a Cu single roll, and T_x of the ribbons was measured by means of DSC, which is one of the conventional thermal analytical methods, at a heating rate of 40 K/min. An amorphous alloy thin film was deposited on glass substrate in vacuum by heating alloy ingots. The thickness of the film was measured by using a surface profilometer using a stylus. The as-prepared ribbons and thin film are amorphous, as no sharp diffraction peaks are found in their X-ray diffraction (XRD) patterns. In-situ measurement of energy dispersive X-ray reflectivity of the film on heating in a N_2 gas flow was performed by using white X-ray and a pure Ge type solid state detector (SSD) at BL-3C in Photon Factory, KEK. The grazing incidence angle and reflection angle were fixed at 0.2° and 0.4°, respectively. The cross sections of the incident and reflected X-ray are 50 × 120 μm^2 and 25 × 50 μm^2, respectively. X-ray reflectivity was measured for 8 s every 10 s. The film was crystallized during the in-situ X-ray reflectivity measurement, because diffraction peaks from crystalline phases are found in an XRD pattern recorded after the reflectivity measurement.

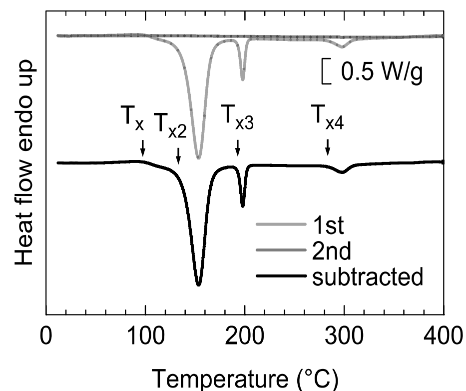

Fig. 1 DSC traces of the Pd-based amorphous melt-spun ribbons measured at a heating rate of 40 K/min.

3. RESULTS AND DISCUSSION

Fig. 1 shows the DSC traces of the Pd-based amorphous alloy ribbons. Exothermic peaks were observed at different four temperatures. Among them, the first exothermic peak is associated with crystallization. Thus, T_x is 99 °C. The peak temperature of the largest exothermic heat flow is 154 °C. It was revealed by EPMA that the difference of the composition between the Pd-based amorphous ribbons and thin film is within about 5 atomic percent. The thickness of the thin film measured by the surface profilometer is about 120 nm.

Fig. 2 shows the X-ray reflectivity measured in the present study. The white X-ray spectrum for BL-3C was measured with Al attenuator whose thickness is 10 mm and is also shown in Fig. 3. The specimen was heated up at a heating rate of 10 − 20 K/min. The profile of oscillations of the reflectivity changes at about 25 keV, corresponding to Pd L-edge absorption. The oscillations are clearly observed even though the photon energy is high at lower temperature than about 140 °C. However, they become faint for higher photon energy region, with increasing temperature. As Albertini et al. [1] mentioned, the thickness of the thin film can be estimated from the distance of scattering parameter between the peaks of the oscillations, Δq. Scattering parameter, q, is defined as

$$q = \frac{4\pi \sin\theta}{\lambda},$$

where θ is the grazing incidence angle and λ is the wavelength of X-ray photons having energy E. The relationship between E and λ is

$$E = h\frac{c}{\lambda},$$

where h is Planck's constant and c is the speed of light. The thickness, d, of the thin film is obtained as

$$d = \frac{2\pi}{\Delta q}.$$

In the present study, the energy resolution of the SSD used is 48 eV. When the energy distance of the peak of the oscillations is 1500 eV or 1548 eV, the film thickness is 118.4 nm or 114.7 nm. Thus, spatial resolution is 3.7 nm.

Fig. 4 shows the calculated film thickness as a function of temperature for the oscillations whose photon energy is higher than Pd L-edge. The film thickness was 130 nm approximately when the temperature was lower than 140 °C, while it was about 127 nm for higher temperature than 140 °C. It seems that this change in the film thickness is discrete. The decrease in the film thickness upon heating means increase in the density of the film. Therefore, it is considered that the discrete change in the film thickness was caused by crystallization and that the crystallization temperature is about 140 °C.

As shown in Fig. 1, T_x of the Pd-based amorphous alloys used in the present study is 99 °C and is 40 K lower than the crystallization temperature measured by X-ray reflectivity. However, this difference is reasonable, because the temperature of the film was not monitored at the same place where the incident white X-ray is irradiated and because the composition of the film is not exactly the same with that of the ribbons. For more precise analysis of the reflectivity, calculation of the profiles of energy dispersive X-ray reflectivity should be

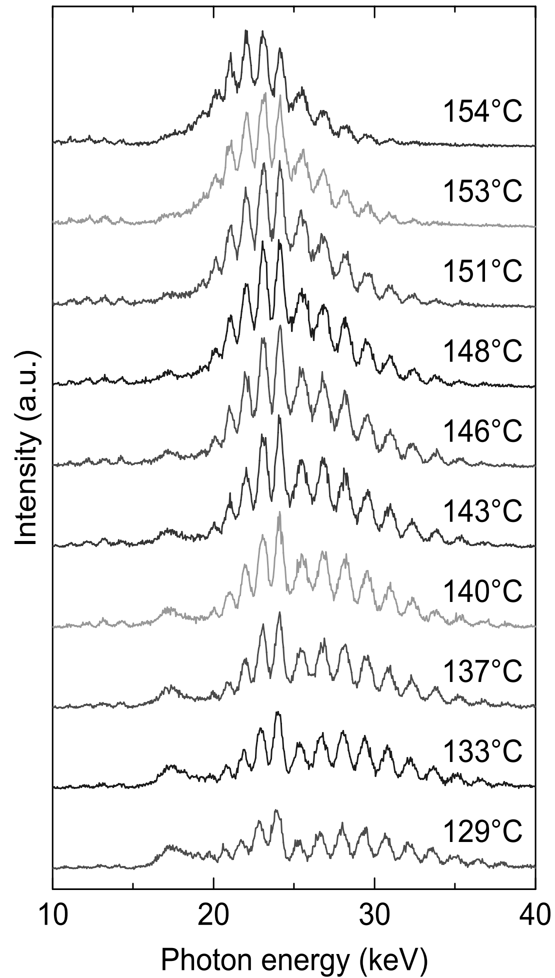

Fig. 2 Energy dispersive X-ray reflectivity of the Pd-based amorphous alloy thin film upon heating. The profiles were measured every 10 s. The grazing incident angle was fixed to 0.2°.

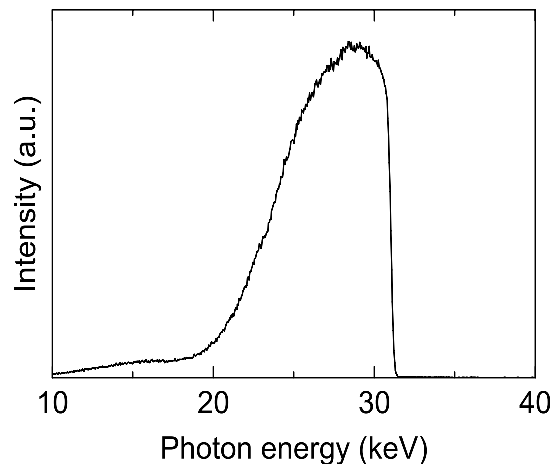

Fig. 3 White X-ray spectrum measured using Al plate which is 10 mm in thickness.

carried out by using a model proposed by Albertini et al. [1] in order to determine the film thickness.

4. CONCLUSIONS

Measurement of crystallization temperature of the Pd-based amorphous alloy thin film was demonstrated by energy dispersive X-ray reflectivity upon heating using white X-ray and SSD. The thickness of the Pd-based amorphous alloy thin film was decreased with increasing temperature. The crystallization temperature of the Pd-based amorphous alloy thin film was about 140 °C.

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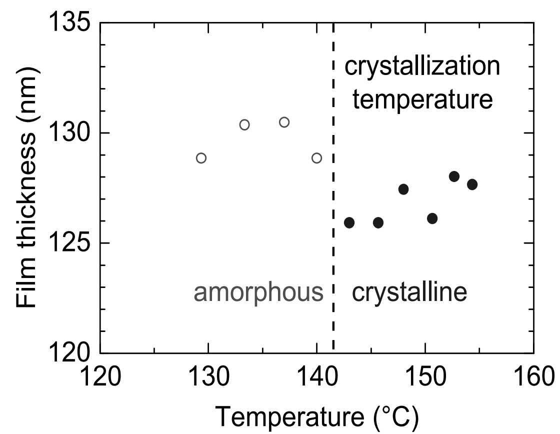

Fig. 4 The film thickness as a function of temperature.

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