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Solid-State Reaction and Vacancy-Type Defects in Bilayer Fe/Hf Studied by the Slow Positron Beam

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Abstract

The positron annihilation lifetimes and the Doppler broadening by slow positron beam are measured in thin Fe films with thickness 500 nm, a thin Hf film with thickness 100 nm, and the bilayer Fe (50 nm)/Hf (50 nm) on quartz glass substrate. We have analyzed the behavior in vacancy-type defects in each layer through some deposition temperatures and annealing. It is observed that the thin Fe film, the thin Hf film, and the bilayer Fe (50 nm)/Hf (50 nm) already contain many vacancy-type defects. We have investigated the change of densities of the vacancy-carbon complex and the small vacancy-cluster with carbons, through solid-state amorphization of Fe (50 nm)/Hf (50 nm) bilayer.

Keywords

Metallic Films, Positron Annihilation Measurement, Solid-State Reaction, Fe Film, Diffusion, Vacancy-Type Defects

1. Introduction

Schwarz and Johnson [1] first have reported that isothermal annealing of thin film multilayers of two different crystalline metals (La and Au) can lead to the formation of an amorphous alloy. There exists a series of systems, mostly on the basis of one of the early transition metals and one of the late transition metals, in which the amorphous systems based on Hf and Zr have the advantage of a higher glass transition temperature. In addition, amorphization by mechanical alloying, a kind of solid-state amorphization, has been discovered [2].

It has been proposed that a multilayer structure, which is created in the initial stage of mechanical allying, plays an important role in amorphization [3]. The anomalously fast diffusion of one component and a large negative heat of mixing in the alloy are important factors in solid-state amorphization [4].

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Oguchi *et al*. [5] have studied the solid-state amorphization in Cu/Hf mutilayers by time different perturbed angular correlation (TDPAC). TDPAC and slow positron beam technique have shown that a strong distortion exists and many vacancy-type defects are present in the Hf layers of Cu/Hf multilayers [6] [7]. Oshima *et al*. [8] have studied the solid-state amorphization in Ni/Hf multilayers by slow positron beam technique. It has been shown that a high density of vacancy-type defects in Hf layers strongly induces a fast diffusion of Ni atoms, which promotes the solid-state amorphization. Fe/Hf multilayers, which have a soft magnetic property, have intensively been studied for high saturation magnetization and high density recording head materials [9]-[14]. A reason for the good magnetic softness is that these multilayers are in the nanocrystalline structures resulting in decreasing magnetocrystalline structure, suppressing the growth of columnar Fe grains have been required. In addition, thermal stability of these multilayers is very important, because most of magnetic heads are fabricated by glass bonding at high temperature. The growth of Fe grains and formation of amorphous-like interfacial product phase with the solid-state reaction between Fe and Hf layers are strongly related to the presence of vacancy-type defects in each layer. The variable energy slow positron beams have enabled studies of atomic vacancy-type defects at the surface, in the near surface, and in thin films [8] [15]-[19]. Especially the lifetime method with slow positron beam can supply the important information, that is, what kind of vacancy-type defects is contained in the thin films [20] [21]. In this study, we have performed the lifetime and the Doppler broadening measurements with the variable energy slow positron beams for the thin Fe film (500 nm), the thin Hf film (100 nm), and the thin bilayer Fe (50 nm)/Hf (50 nm), and have investigated the nature of the vacancy-type defects in these thin films.

2. Experimental Method and Analysis

The specimens were deposited by an MBE method using two electron gun sources for Fe and Hf. The MBE chamber was brought into the 10-10 Torr range prior to deposition. Thin Fe films of thickness 500 nm were deposited on the quartz glass substrate at room temperature and 473 K. A thin Hf film of thickness 100 nm was deposited on the quartz glass substrate at room temperature. In the case of Fe/Hf bilayers the Hf layer of thickness 50 nm was deposited on a quartz glass substrate at room temperature and subsequently the Fe layer of thickness 50 nm was deposited on the Hf layer at room temperature. The incident positron energy E was variable from 0 to 13 keV. The measurements of Doppler broadening spectra by slow positron beam were carried out at room temperature with a high purity germanium detector. In order to estimate the vacancy-type defects in these thin films the S-parameter was used. S was determined by the ratio of the central area over 10 channels to the total area of the positron annihilation photopeak spectrum after subtracting the background.

The positron annihilation lifetime measurements by slow positron beam were carried out at room temperature by use of the positron pulsing system with an intense slow positron beam generated by an electron linac in the National Institute of Advanced Industrial Science and Technology (AIST) LINAC facility. The lifetime spectra were obtained by measuring the time interval between the timing signal derived electrically from the pulsing system and the timing signal of an annihilation γ-ray detected with a BaF2 scintillation detector. The detailed lifetime measurement system is described elsewhere [22]. For each spectrum, at least 3.0 × 105 counts were analyzed using the "RESOLUTION" routine [23] with good variance of the fits with a time resolution of about 290 ps FWHM.

In the present study, we used the scaling method [24] [25] for analyzing the positron implantation profiles in these thin films. Taking into account the diffraction effect of positron around the interfaces in multilayers, the scaling function of the positron implantation profile is represented as follows:

$$\tilde{P}(E,z) = \frac{\langle z(E)\rangle_i N_p(E) P(E,z)}{\left[1 + A_{i,i-1}(E,z) + A_{i,i+1}(E,z)\right]} \tag{1}$$

$$= N_{lm}\left(\frac{u}{C_{lm}}\right)^l \exp\left[\left(\frac{u}{C_{lm}}\right)^m\right] \tag{2}$$

where

$$u = \frac{(z - d_{i-1})}{\langle z(E)\rangle} + \sum_{j=1}^{i=1} \frac{d_j - d_{j-1}}{\langle z(E)\rangle_j} \tag{3}$$

and d_i is the length from the surface to the i th-layer. N_{im} is a normalized constant, C_{im}, l and m are parameters which depend on the materials. $\langle z(E)\rangle$ is a mean implantation depth. The atomic number dependence of these parameters has already been obtained [24] [25].

The parameter $N_p(E)$ and A are found to depend on the atomic number of the constituent elements, from Monte Carlo simulations [25]

$$N_p(E) \equiv \frac{\left[1 + A_{i,i-1}(E,z) + A_{i,i+1}(E,z)\right]}{\int_0^\infty \mathrm{d}z\tilde{P}(E,z)} \tag{4}$$

$A_{i,i-1}(E,z)$ and $A_{i,i+1}(E,z)$ are represented as follows:

$$A_{i,i-1}(E,z) = \left(\eta_{i-1}^+ - \eta_i^+\right)\exp\left[-\frac{(z-d_{i-1})}{\langle z(E)\rangle_i}\right] \tag{5}$$

$$A_{i,i+1}(E,z) = \left(\eta_{i+1}^+ - \eta_i^+\right)\exp\left[-\frac{(d_{i-1}-z)}{\langle z(E)\rangle_i}\right] \tag{6}$$

$$\eta_i^+ = b_1 - b_2\exp\left[-b_3E\right] \tag{7}$$

where b_1, b_2 and b_3 are parameters, which are represented as function of the atomic number of materials.

3. Results and Discussions

Figure 1(a) shows the measured *S*-parameters versus the incident positron energy for the bilayer Fe (50 nm)/Hf (50 nm) on quartz glass substrate with the bilayer thickness $\lambda \sim 100$ nm. The closed circles show the values of *S*-parameter for the bilayer, which is deposited on quartz glass substrate at room temperature and subsequently the Fe layer (50 nm) is deposited on Hf layer at room temperature. The open circles show the values of *S*-parameter for the bilayer annealed for 2 hours at 800 K. The double circles show the values of *S*-parameter for the bilayer annealed for 4 hours at 800 K.

Figure 1(b) shows the implantation profiles in the bilayer Fe (50 nm)/Hf (50 nm) on the quartz glass substrate for some incident positron energies. It is found that the values of *S*-parameter in the bilayer Fe (50 nm)/Hf (50 nm) annealed for 2 hours at 800 K decrease remarkably in the region of the incident energy from 2 to 3 keV, in comparison with those of as-deposited bilayer.

From the positron implantation profiles in **Figure 1(b)**, it is seen that the *S*-parameter in the region from 2 to 3 keV reflects the property of the Fe layer dominantly. This means that vacancy-type defects in the Fe layer annihilate dominantly and vacancy-type defects in the Hf layer do not change much during annealing for 2 hours at 800 K.

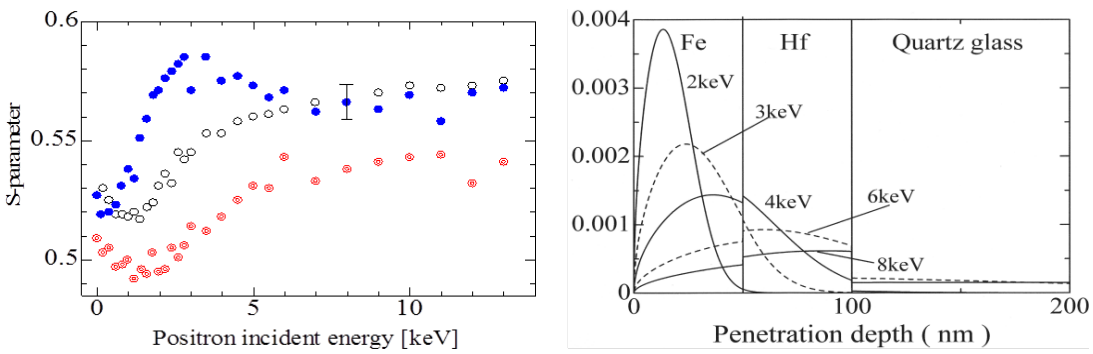

Figure 1. (a) *S*-parameter vs. incident positron energy for the bilayer Fe (50 nm)/Hf (50 nm); (b) The positron implantation profiles in the bilayer Fe (50 nm)/Hf (50 nm) at some incident energies.

Furthermore, it is found that the values of *S*-parameter in the bilayer annealed for 4 hours at 800 K decrease much in the region of the incident energy from ~0 to ~13 keV, in comparison with those of as-deposited bilayer. This indicates that vacancy-type defects in both Fe and Hf layers annihilate much during annealing for 4 hours at 800 K. These results show that diffusion of Fe component is much faster than that of Hf component. This corresponds to one of important factors in solid-state amorphization [4].

Figure 2 shows the positron annihilation lifetimes and those intensities in the thin Fe film of the thickness 500 nm, which is grown on the quartz glass substrate at room temperature and 473 K, and the lifetimes and intensities in the thin Hf film of the thickness 100 nm, which is grown on the quartz glass substrate at room temperature. The positron incident energies are 6 and 3 keV in the case of the Fe films and the Hf film, respectively. The lifetime, ~332 psec., in the thin Fe film of thickness 500 nm, which is grown at room temperature, corresponds to vacancy-clusters, which contain carbon, compose of vacancies from ~5 to ~10 numbers [26]-[30]. On the other hand, the lifetime, ~166 psec., in the thin Fe film of thickness 500 nm, which is grown at 473 K, corresponds to the single-vacancies [26] [27], which might be trapped on carbon impurity atoms [29] [30], because single-vacancies move frequently in pure Fe at room temperature [31] [32]. The lifetime, ~232 psec., in the thin Hf film of thickness 100 nm corresponds approximately to the single-vacancy [26].

Figure 3 shows the positron annihilation lifetimes and those intensities versus the incident positron energy for the bilayer Fe (50 nm)/Hf (50 nm) after annealing for 4 hours at 800 K. The lifetimes 277 psec. (the incident positron energy 2 keV) and 250 psec. (the incident positron energy 3 keV) correspond to vacancy-clusters composed of vacancies from 4 to 5 numbers. Now we shall consider interfacial reactions and growth of the interfacial product amorphous-phase. The free enthalpy, whose T is temperature, is given for the amorphous Hf_xFe_{1-x} interfacial produce phase, assuming additivity of the specific heat as follows,

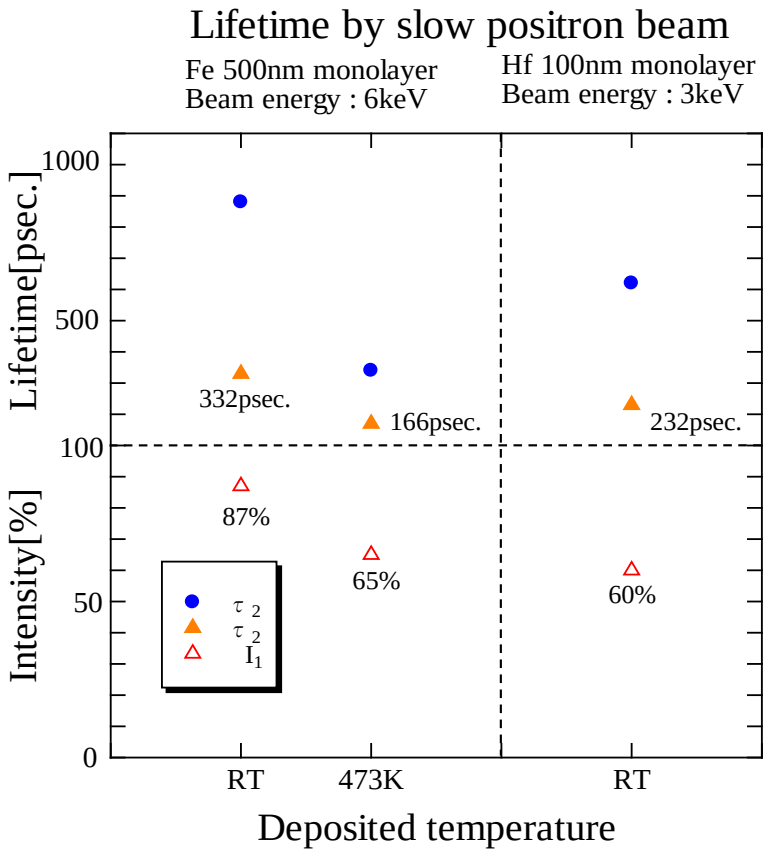

Figure 2. The positron annihilation lifetimes and those intensities in the thin Fe film of the thickness 500 nm at room temperature and 473 K, and the lifetimes and intensities in the thin Hf film of the thickness 100 nm at room temperature.

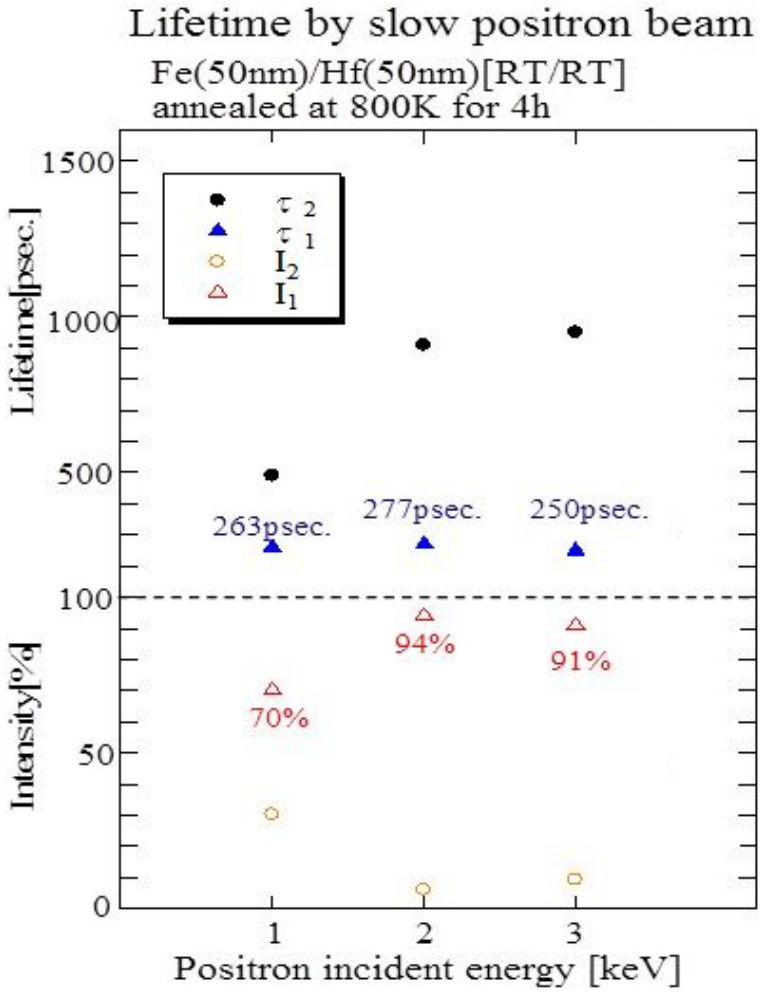

Figure 3. The positron annihilation lifetimes and those intensities vs. the incident positron energy for the bilayer Fe (50 nm)/Hf (50 nm) after annealing for 4 hours at 800 K.

$$G(x,T) = xG^{\mathrm{Hf}}(T) + (1-x)G^{\mathrm{Fe}}(T) + \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}$$

$G^{\mathrm{Hf}}(T)$ and $G^{\mathrm{Fe}}(T)$ are the free enthalpies of Hf layers and Fe layers, respectively.

ΔH_{mix} is the enthalpy of mixing.

ΔS_{mix} is the entropy of mixing.

The free enthalpy of the amorphous Hf_xFe_{1-x} interfacial product phase is lowered due to the large negative heat of mixing. These terms give a driving force for the interfacial reaction. We must consider why the stable crystalline HfFe alloy phase is not formed at the beginning of the reaction although there is enough mobility to grow the amorphous HfFe interfacial product phase in a diffusion reaction. Kinetic restrictions are necessary so that the transition will not go into the equilibrium state, but instead to the metastable amorphous state. One answer has its basis in the asymmetric mobilities of the two reactants (Fe and Hf). Certainly the present experimental results show that the diffusion of Fe component is much faster than that of Hf component. Thus the smaller late transition metals (Fe, Co etc.) are responsible for the thermally excited mass transport in contrast to the early transition metals (Hf, Zr etc.), which move just out of their equilibrium positions but do not contribute to the diffusion process. Another problem is why the activation energy of the interfacial reaction is much low in comparison with the activation energy (~2.45 eV) [33] for the self-diffusion of Fe in bcc α-Fe. The present experimental results give one answer for this problem. That is, Fe/Hf layers already contain many vacancy-type

defects. In the case of Fe layers, taking account of the carbon-vacancy binding energy (~0.85 eV) [30], the activation energy is estimated to be ~1.40 eV = ~0.85 eV + ~0.55 eV (the vacancy migration energy in Fe) [30]. This value of the activation energy is much lower than the activation energy (~2.45 eV) of the self-diffusion of Fe.

4. Conclusion

We have measured the positron annihilation Dopper broadening in the bilayer Fe (50 nm)/Hf (50 nm) by slow positron beam during the isochronal annealing at 800 K. We have analyzed the changes in density of the vacancy-carbon complex and the small vacancy-cluster, which might contain carbons, through solid-state amorphization of Fe (50 nm)/Hf (50 nm) with the positron annihilation lifetime by slow positron beam. We have discussed what kind of vacancy-type defects exists in Fe (500 nm) layer and Hf (100 nm), respectively.

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