111\textsuperscript{Cd}(\leftrightarrow 111\textsuperscript{In}) Time Differential Perturbed Angular Correlation (TDPAC) Spectroscopy in Fe/Ag Films

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We have investigated the magnetic properties of Cd atoms decayed from 111\textsuperscript{In} at the interfaces of Fe/Ag evaporated films. In order to determine the magnetic properties of the films, we have measured 111\textsuperscript{Cd}(\leftrightarrow 111\textsuperscript{In}) time differential perturbed angular correlation (TDPAC) spectra at room temperature as a function of distance from the interface. Fe and Ag were evaporated using electron beam evaporation, and small amounts of radioactive 111\textsuperscript{In} were evaporated by resistance-heating. The evaporated films had the following stacking orders on kapton polyimide film substrate: (1) polyimide/Fe 50 nm/\textsuperscript{111}In/Fe x nm/Ag 20 nm (x = 0.2, 0.3, 1, 3, 5, 10), (2) polyimide/Fe 50 nm/Ag x nm/\textsuperscript{111}In/Ag 20 nm (x = 0, 0.2, 1). We used an Ag layer as a cap layer in order to prevent oxidation in air. TDPAC spectra were measured using a four-detector arrangement. The hyperfine magnetic field tends to be slightly larger when 111\textsuperscript{In} is close to the interface of the Fe/Ag layer. The intensity of perturbation damps rapidly as 111\textsuperscript{In} is close to the interface of Fe and Ag. These behaviors are thought to depend on electric field gradients and the influence of the surface roughness.

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1. Introduction

The physical properties of a particular localized area, such as a surface or an interface, dictate the nature of a material. In order to understand the nature of a [magnetic/non-magnetic] multilayer, it is necessary to investigate the microscopic nature of the surface and the interface of a magnetic layer with a non-magnetic layer. An effective method for this is to introduce small amounts of a radioisotope as probe atoms into the material for investigating the properties of the interface. The magnetism and local area structure can then be determined through hyperfine interactions (hyperfine magnetic field and electric field gradient) using Mössbauer spectroscopy and time differential perturbed angular correlation (TDPAC) spectroscopy. The purpose of this research is to investigate the surface and interface of an evaporated Fe film microscopically using the 111\textsuperscript{Cd}(\leftrightarrow 111\textsuperscript{In}) TDPAC.

It is thought that the magnetic moment at the surface of a ferromagnetic metal in vacuum is larger than the magnetic moment inside the crystal at low temperatures.\textsuperscript{1,3} It is concluded from theoretical calculations that the magnetization of the ground state (T = 0) increases at the surface of a magnetic metal such as Ni and Fe.

In previous work, the surface of Fe has been investigated by 57\textsuperscript{Fe} Mössbauer spectroscopy,\textsuperscript{2,4} wherein an 57\textsuperscript{Fe} layer was evaporated on the surface of a 57\textsuperscript{Fe} layer for 57\textsuperscript{Fe} Mössbauer spectroscopy. The dead-layer model has been proposed.\textsuperscript{2}

In order to confirm this experimentally, the hyperfine fields of an ultra-thin Fe film (4 atomic layers thick) placed between Ag layers were measured using Mössbauer spectroscopy.\textsuperscript{3,4} The results showed that the hyperfine field is larger at the center of the Fe layer than at the interface at room temperature, and the hyperfine field is larger at the interface of the Fe layer than at the center at low temperatures under about 170 K.\textsuperscript{31}

In order to study the properties of the selected layers in detail, the quantity of the atomic probes needs to be very small. If the quantity of atomic probes is much, we will get the nature of global film. If 57\textsuperscript{Co} is evaporated instead of 57\textsuperscript{Fe}, it is possible to carry out measurements with very small quantities of the probe. However, this is a difficult experiment, because of the long half-life of radioactive 57\textsuperscript{Co}. The half-life of 57\textsuperscript{Co} is 271 days. On the other hand, the lifetime of 111\textsuperscript{In} is 2.8 days, and it is easy to use 111\textsuperscript{In} for the experiments.

Some multilayer films sandwiched between non-magnetic and magnetic layers show giant magnetoresistance. Such films are expected to be used in sensors or as recording head materials. For these, a small difference in magnetic field is converted into an electric signal. It is a major technological hurdle to translate a minute magnetic field change to a large resistance change at room temperature. For improvements and further development of these multilayered films, we need to investigate and understand the magnetism of a layer in detail. The method of evaporation of 111\textsuperscript{In}, in amounts of less than 1 monolayer, can introduce 111\textsuperscript{Cd} probe atoms at a particular position in a film (an interface or a shallow position in a non-magnetic layer, etc.) and the hyperfine interactions of the probe nucleus can clarify the physical properties of the particular position.

2. Experimental Procedure

A very small quantity of 111\textsuperscript{In} was introduced into an Fe film as described below. Fe was first evaporated using an electron beam evaporation method. Then, 111\textsuperscript{In} was evaporated using a resistance heating method. Thus, a Fe/111\textsuperscript{In}/Fe sandwich film was formed. All the experiments were

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performed at the Toyonaka Annex to the Osaka University Radioisotope Center.

We extracted $^{111}$In from a carrier-free $^{111}$In HCl solution. The reason for this is that Cl atoms have an adverse influence on TDPAC spectra. Half of the $^{111}$In HCl solution (74 MBq, 1 mL, Nihon Medi-Physics) was dropped on a Tungsten boat (SF-156W, Nilaco). This $^{111}$In HCl solution contains $^{111}$In (about $4.2 \times 10^{12}$ atoms per 1 mL) and Cd impurities ($^{109}$Cd, $^{111}$Cd, etc.; less than about $1.1 \times 10^{15}$ atoms per 1 mL) at the time of delivery as a result of the production process. The $^{111}$In HCl solution was dried to $^{111}$InCl, using infrared light. The W boat with $^{111}$InCl, was covered with another W boat facing each other. Both ends of the W boats were attached using Pt wire. We placed the boats in an atmosphere of Ar + 7% H$_2$ (purity of Ar: 99.99%, H$_2$: 99.9%) after forming a vacuum in the silica tube containing the W boats. The boats were heated to 873 K using an infrared image furnace. The temperature was raised for 30 min and was then maintained at the specified temperature for 5 min. $^{111}$In and $^{111}$InCl$_2$ melt at 873 K (the melting point of InCl$_2$: 498 K, InCl$_3$: 508 K, InCl$_4$: 859 K, In: 430 K, sublimation point of InCl$_3$: 859 K). $^{111}$In remained on the upper W boat since In tends to wet W. Cl$_2$ from $^{111}$InCl$_2$ flowed with the Ar + 7% H$_2$ gas to the gas flow outlet. After heating, the radioactivity of $^{111}$In and $^{111}$InCl$_2$ on the W boats were measured from a distance of 5 cm using a $\gamma$-ray Geiger-Muller (GM) survey meter (TGS-133, Aloka). The radioactivity of the $^{111}$In on the upper W boat and the radioactivity of the $^{111}$InCl$_2$ on the W boat on the lower side measured by the GM tube was about 0.1–0.2 MBq, respectively. However, this is a referential value, since the GM tube is only able to calculate hundreds of Bq precisely for its dead time. The remaining $^{111}$In and $^{111}$InCl$_2$ were found on the silica tube.

Polyimide/Fe 50.0(1) nm/$^{111}$In/Fe x nm/Ag 20.0(1) nm (x = 0.2(1), 0.3(1), 1.0(1), 3.0(1), 5.0(1), 10.0(1)) multilayers, which were used in this study, were prepared using the following evaporation conditions. The purities of Fe and Ag were 99.999% and 99.999%. The Fe and Ag ingots were prepared using the traditional quartz vibrator method. In the same way, we made other evaporated films: polyimide/Fe 50.0(1) nm/Ag x nm/$^{111}$In/Ag 20.0(1) nm (x = 0.2(1), 1.0(1)).

At room temperature, all TDPAC measurements were performed without the application of an external magnetic field. The films were cut and divided into 5 × 5 mm$^2$ squares, and set parallel to the detector plane. However, in the case of the TDPAC measurement at 22 K, performed using a He gas cryostat, the film was placed perpendicular to the detector plane and an external magnetic field was applied (0.25(1) T) using permanent magnets (NEOMAX, height: 5 mm, diameter: 6 mm).

We measured TDPAC of polyimide/Fe 50.0(1)/$^{111}$In/Fe x nm/Ag 20.0(1) nm (x = 3.0(1), 10.0(1)) after annealing at 473 and 673 K for 30 min using a Gold image furnace in an atmosphere of Ar + 7%H$_2$. We also prepared the following films and measured TDPAC: polyimide/Fe 50.0(1)/$^{111}$InCl$_2$/Fe 10.0(1) nm/Ag 20.0(1) nm, and polyimide/Fe 50.0(1)/O/$^{111}$In/Fe 10.0(1) nm/Ag 20.0(1) nm. In addition, we also prepared and measured TDPAC from bulk Fe containing isolated $^{111}$In probe atoms using an arc furnace.

The $^{111}$Cd($^{\gamma}$,$^{111}$In) isotope is the best known nucleus for TDPAC measurements in materials science$^5$ and has a suitable half-life at an intermediate state of $t_1/2 = 85.0$ ns. TDPAC measurements were performed with the well-known
171.3–245.4 keV $\gamma-\gamma$ cascade, successively emitted from $^{111}$Cd, using a conventional four-detector arrangement in a plane with 90 degree angular separations. Photomultiplier tubes (XP2020Q, Philips) mounted BaF$_2$ scintillators (cylinder form with diameter 1.5 inch, height 1 inch, OKEN) were used.

3. Results and Discussion

TDPAC measurements were performed at room temperature using a four-detector measurement arrangement. We can obtain the perturbation function $R(t)$ using the following equation, from eight time spectra, $C_{ij}$:

$$R(t) = 2 \left( \frac{C_{13}C_{24}C_{31}C_{42}}{(C_{13}C_{24}C_{31}C_{42})^{1/4} + 2(C_{14}C_{23}C_{41}C_{32})^{1/4}} \right)$$

(1)

$C_{13}, C_{24}, C_{31}, C_{42}$ are the time spectra of the angular correlations obtained with the counter set at 180°. $C_{14}, C_{23}, C_{41}, C_{32}$ are the time spectra of the angular correlation that are obtained at 90°. When there is a magnetic field vertical to the plane including the sample and the detectors, the left side of eq. (1) is given as follows:

$$R(t) = a_0 + a_1 \cos(2\omega_0 t)$$

(2)

Here, $a_0$ and $a_1$ are coefficients, and $\omega_0$ is a Larmor frequency. If the directions of the magnetic moment are random, such as in a powder pattern, eq. (1) becomes:

$$R(t) = a_0 + a_1 \cos(\omega_1 t) + a_2 \cos(2\omega_1 t)$$

(3)

If we suppose that the Larmor frequency has a Gaussian distribution, eqs. (2) and (3) become:

$$R(t) = a_0 + a_1 \exp(-2\delta_0^2 t^2) \cos(2\omega_1 t)$$

(4)

$$R(t) = a_0 + a_1 \exp(-\delta_0^2 t^2) \cos(\omega_1 t) + a_2 \exp(-2\delta_0^2 t^2) \cos(2\omega_1 t)$$

(5)

Here, $a_0$ and $a_1$ are coefficients, and $\exp(-\delta_0^2 t^2)$ is the damping factor when $\omega_1$ is the Gaussian distribution.

If a perturbation is due to a quadrupole interaction, and the spin of the intermediate state is 5/2, then:

$$R(t) = a_0 + a_1 \exp(-\delta_0^2 t^2) \cos(\omega_1 t) + a_2 \exp(-\delta_0^2 t^2) \cos(\omega_2 t) + a_3 \exp(-\delta_0^2 t^2) \cos(\omega_1 + \omega_2) t$$

(6)

Here, $a_0, a_1, a_2$ and $a_3$ are coefficients, $\omega_1$ and $\omega_2$ are related to the quadrupole frequencies, and $\exp(-\delta_0^2 t^2)$ expresses damping when $\omega_0$ is the Gaussian distribution. In this paper, we do not discuss the electric field gradient and details of the theory regarding the electric field gradient are given in another paper. 5)

The TDPAC spectra of Fe/Ag containing $^{111}$In in an Fe layer can be fitted to a pure magnetic interaction pattern expressed by eq. (5), and the spectra of Fe/Ag containing $^{111}$In at the interface. Similarly, the spectra in an Ag film can be fitted to a pure electric quadrupole interaction pattern, which is expressed by eq. (6). The spectra were fit by one kind of Larmor frequency, and this means that there is a predominant component in the observed spectra. We can satisfactorily obtain the value of the hyperfine magnetic field except for the influence of the electric field gradient that appeared until about 10 ns in the PAC spectra [Figs. 2(a), (b), (c), (d), 3(a), (b), (c)]. The spectrum of the Fe/Ag film measured at 22 K was fitted using eq. (4) that contains only 2 times the Larmor frequency, because the magnetic moments are aligned by the external magnetic field which is perpendicular to the 4 detector plane. The spectrum of isolated $^{111}$In in the bulk Fe was fitted using eq. (5).

The Larmor frequency, $\omega_L$, is proportional to a hyperfine magnetic field $H$ as given below:

$$\omega_L = -\frac{g_N\mu_N H}{\hbar}$$

(7)

Here, $g_N$ is a g-factor ($-0.306$ for $^{111}$Cd), and $\mu_N$ is a nuclear magneton.

We can consider the PAC spectra of polyimide/Fe 50 nm/$^{111}$In/Fe x nm/Ag 20 nm ($x = 0.2, 0.3, 1, 3, 5, 10$) together with the power spectra, Fourier-transformed using a maximum entropy method (Figs. 2, 3). As $^{111}$In is introduced close to the interface, the intensity of the PAC spectrum is weak. This is because of an electric field gradient and the
influence of the turbulent Fe/Ag interface. When there are various $^{111}$In sites, the spectrum is the sum of the cosine curves of the various frequencies, and the intensity of the spectrum decreases. An Fe layer and a Ag layer form the interface, and slight atom mixing at the interface might occur. Also, lattice strains are induced in the crystal structure since the Cd atom has a larger atomic size and the lattice constants of Fe and Ag are different.

We now consider the PAC spectra of samples containing $^{111}$In at a deep location in relation to the Fe/Ag interface (Fig. 2). These are the samples containing $^{111}$In in the Fe layers at 1, 3, 5, and 10 nm from the Fe/Ag interface. When compared to the PAC spectrum of the $^{111}$In isolated in bulk Fe, they show the same trend as the spectrum for $^{111}$In in the bulk. In these spectra, the component of a Larmor frequency and the component of 2 times the Larmor frequency are different from the Fe/In/Ag interface, even though $^{111}$In is present in a very small amount, less than a monolayer. The low frequency component is thought to correspond to the component of an electric field gradient. The high frequency components, other than the Larmor frequencies, depend on mechanical noise. This noise is common to other spectra as well.

The hyperfine magnetic field as a function of the distance from the Fe/Ag interface is shown in Fig. 4. Hyperfine fields of $^{111}$In are slightly larger in the Fe film with $^{111}$In 0.2 nm from the interface than in the bulk Fe. From the results of fitting the spectra (Figs. 2, 3) in the range of 20–100 ns to minimize the influence of the electric field gradient and mechanical noise, the hyperfine fields of $^{111}$In in the Fe film 0.2 nm from the interface is calculated to be 38.9(3) T and the hyperfine field of $^{111}$In in the bulk Fe is 38.0(1) T.

Mössbauer spectroscopy of the Fe/Ag film was carried out in a previous study. This is the experiment that measured the Mössbauer spectra of Fe/Ag film at a low temperature, using a $^{57}$Fe layer as the probe. The hyperfine magnetic field even in the present study became large near the Fe/Ag interface. However, the previous study was performed at a low temperature, therefore a direct comparison is not possible. Freeman has reported a theoretical study in a Fe/Ag film at a low temperature. A hyperfine magnetic field becomes large at the interface of the Fe/Ag film at a low temperature.
temperature. However, it is thought that a hyperfine magnetic field becomes small at room temperature. When the temperature is high, the exchange field fluctuates. An Fe–Ag interface containing In is different from the Fe–Ag interface since In is larger than Fe. If a Fe/Ag film is measured at a low temperature, we can examine the consistency of the experimental results at a low temperature compared to past theoretical and experimental studies. However, there have been only few measurements at low temperatures thus far.

In the present study, we performed measurements at 22 K (Fig. 5). A film was placed vertical to the detector plane and an external magnetic field (0.25(1) T) was applied in parallel to the film. The reason for applying an external magnetic field is that only the 2 times Larmor frequency component can be observed. The frequency became large because of the measurement at low temperature. The hyperfine field is 40.7(6) T as calculated from the results of fitting and subtracting the external magnetic field. For comparison, the hyperfine field at room temperature is 38.3(2) T.

We now consider the TDPAC spectra of the sample containing $^{111}$In at the Fe/Ag interface and the sample containing $^{111}$In in the Ag layer (Fig. 6). The component of the Larmor frequency due to the hyperfine magnetic field from Fe is not clearly seen in these spectra. Only the low frequency component due to the electric field gradient can be seen. From this result, it can be concluded that there is no influence of the hyperfine magnetic field derived from Fe at the Fe/Ag interface and in the Ag layer.

The TDPAC was also measured after the evaporated film was annealed at 473 and 673 K for 30 m in a Gold image furnace in an atmosphere of Ar + 7%H$_2$. When films are produced, the temperature of the substrate is maintained at room temperature. Therefore, some defects and dislocations are present in them. The decrease in the amplitude in the PAC spectra became small after the film was annealed. This suggests that some defects and dislocations were removed after the annealing treatment. Prior to annealing, there are various states of $^{111}$In depending on the defects and dislocations present. Thus, the distribution of the frequencies is broad in the frequency spectra. As a result of annealing, some defects and dislocations decreased, and the number of the states of $^{111}$In decreased. However, the state does not change much by annealing after evaporation.

4. Conclusions

We produced an evaporated thin film of polyimide/Fe 50 nm/$^{111}$In/Fe x nm/Ag 20 nm ($x = 0, 0.2, 0.3, 1, 3, 5, 10$ nm etc.). The amplitude of a PAC spectrum became weak with the introduction of $^{111}$In close to the interface. This is due to the fact that the interface is turbulent. On the other hand, hyperfine fields are slightly larger for $^{111}$In in the Fe bulk (38.0(1) T) to $^{111}$In 0.2 nm from the interface (38.9(3) T). The component of the Larmor frequency due to the hyperfine magnetic field from Fe is not seen clearly in the spectra of the sample containing $^{111}$In at the Fe/Ag interface and the sample containing $^{111}$In in the Ag layer.

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REFERENCES