유리 위에 증착된 다결정 Fe 자성박막의 이차조화파 회전 이방성

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유리판 위에 증착된 다결정 Fe 자성박막의 두께에 따른 표면 결정 구조가 Ti:Sapphire 레이저를 사용하여 조사되었다. 비선형 광학 유전율의 결정구조에 따른 대칭성에 대한 계산으로부터 박막 표면은 C_{2v} 에 매우 가까운 C_s 구조를 갖음을 보였다. 이러한 광학적 회전 이방성은 임의 방향의 그레이너드로 구성된 다결정 구조의 박막에서는 매우 이례적인 일이다. 이차조화파로부터 얻은 이 결과는 (110) bcc 형태로 자란 X선 회절 결과와도 일치하는 것으로 매우 얇은 상태 일 때 가지고 있던 박막 표면의 등방 구조가 두께가 증가함에 따라 바뀌면서 bulk 상태의 구조를 점차적으로 갖게 됨을 보여주고 있다.

주제어 : 이차조화파, 다결정 Fe 박막, 회전이방성

Second Harmonic Rotational Anisotropy of Polycrystalline Fe Films on Glass Substrates

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The surface structure of polycrystalline Fe films of various thicknesses on glass substrates have been studied using a Ti:Sapphire laser at 780 nm. We found that the surface structure possesses C_s crystal structure close to C_{2v} through symmetry consideration. We present one-fold intensity profile with one mirror plane in second harmonic (SH) intensity as a proof of C_s symmetry. C_s and C_{2v} surface symmetries usually appear at the (110) surface of a cubic diamond single crystal [1]. Therefore this surface symmetry would be related to bcc (110) growth orientation coinciding with XRD measurement. Further we treated surface normalized SH asymmetry with various thicknesses. The SH asymmetry increases with increasing of film thickness. From these results, it is observed that the surface structure of thin polycrystalline Fe film below 5 nm is almost isotropic, while in the case of the thicker Fe films, surface structure have C_s symmetry structure close to C_{2v} .

Keywords : second harmonic generation, Fe, rotational anisotropy

I. Introduction

Optical reflected second-harmonic generation (SHG) has been verified to be a useful tool to analyze structural and electronic properties at the surface and interface of centrosymmetric materials. Especially high symmetry such as surface of single crystal material has been thoroughly studied. However, most crystalline materials used in tech-

nological applications are polycrystalline materials rather than single crystals [2-4]. Many previous studies for polycrystalline materials have been mainly focused on average surface thermodynamic properties, grain boundary energy and structure [5-7]. The study on surface structural property has a great importance in fabrication of the spintronic devices which require well-defined surfaces for spin injection and transport.

In this paper, SHG measurement is implemented to find the surface structure of polycrystalline Fe film growth on

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Fig. 1. Schematic diagram for second harmonic rotational anisotropy measurement.

glass substrate showing bcc (110) growth orientation. We proved that the surface structure possesses C_s symmetry through calculating susceptibility tensors with SHG intensity at macroscopic size. In the case of (110) surface for the lowest symmetry class such as diamond of the cubic there can exist two symmetry classes, C_s and C_{2v} . SH intensity from (110) surface showing C_{2v} symmetry is already reported [1]. Here we prove that the surface of thick Fe film has a crystal symmetry closer to C_s by calculating normalized SH asymmetry with increasing thickness. A comparison between SH intensities of polycrystalline material and XRD data would supply further understanding on characteristics of the thin film growth.

II. Experiment

We used a SHG system to measure the surface structure of ferromagnetic Fe films on glass a substrate at a macroscopic size. This SHG setup consists of pulse laser, polarizer and analyzer, lenses, filters and photomultiplier tube (PMT). The detailed setup and measurement geometry are shown Fig. 1. We used femto-second terawatt Ti: Sapphire laser, mode-locked at 780 nm, the center of wavelength as a pulse laser and Nd: YVO4 (Spectra, Millennia Vs J) continuous laser as a pumping laser, which is capable of stable 5 W pumping at 532 nm. We controlled incident power by using the half-wave plate and the polarizer to protect sample from possible damage by a focused laser spot. The SH intensity from Fe sample at specified incident polarization at 0~130 mW to obtain information on normalized SH asymmetry. The value of the full width at half maximum (FWHM), measured right after the output coupler of the Ti: Sapphire oscillator, was

Fig. 2. X-ray diffraction pattern for polycrystalline Fe film.

about 80 nm. The mode-locked laser power was in the range of 230~250 mW with 10- to 30-fs pulse width and a repetition rate of 82 MHz. The filters located on both sides of a sample were used to block unexpected SH wave from optical elements and the filter behind sample is for blocking fundamental wave, respectively.

Polycrystalline Fe films were grown on glass substrate at 300 K with DC magnetron sputtering system. Ar gas pressure was 5 m Torr during deposition under base pressure at 2×10^{-6} Torr. We covered Si_3N_4 was capped on the polycrystalline Fe to refrain from surface oxidation.

III. Results and Discussion

The surface and interface break inversion symmetry, and SH signal is caused by inversion symmetry breaking.

Fig. 3. Rotational anisotropy of SH intensities for different polarization configurations.

If the sample has not a single domain, grain boundary also contributes to SH intensity. It was reported SH intensity is more productive at the grain boundary than at the surface of poly-silicon [8, 9]. When we compared polycrystalline and single crystal Fe films, SH intensities were almost same. Therefore we believe that grain boundary does not affect SH intensity for all the samples in this paper.

We measured X-ray patterns with various thicknesses. It is experimentally proven that polycrystalline Fe on glass substrate has a strong preference of (110) and a weak (211) growth orientation as shown in Fig. 2 coinciding with reported data [2]. Furthermore, Fig. 3 shows the

surfaces structure is anisotropic. Even though a mixture of randomly oriented grains behaves evidently as an isotropic substance, these Fe films behave like an anisotropic substance both at the surface and in the bulk. It should be noted that there can be a difference between the surface and growth orientation. From Fig. 3 we can get the surface structure of the samples through symmetry operators. We measured SH intensity by azimuthal rotation of the sample a stage (see Fig. 1). There are four selected configurations. Frequency-doubled s-polarized output is almost comparable with the noise due to dark current. SH intensity is negligible for ss (the former letter corresponds to the

polarization of fundamental beam and the latter to the polarization of second harmonic beam) and for ps configurations. The each p-output data shows that there is one mirror plane for frequency-doubled output. SH intensities for sp and pp configurations have 65° and 120° inclined mirror plane, respectively. From these rotational anisotropy data surface crystal symmetry can be determined. For the 32 crystal class, there are 21 noncentrosymmetric crystal classes and 11 centrosymmetric including $\bar{1}$. And there are only three crystal classes C_s , C_{3h} and D_{3h} including $\bar{2}_z$ not $\bar{1}$, where an n -fold rotation-inversion axis, denoted by n , corresponds to the rotation of an object through an angle of $360/n^\circ$ followed by inversion through a fixed point. Considering one-fold behavior of SH intensities polycrystalline Fe on glass substrate showing (110) growth orientation would possess one of the C_s , C_{3h} and D_{3h} crystal classes. Additionally, since the form of the SH profile is approximately $A + B\sin\phi$, C_s or C_2 are the possible classes which films can have. Therefore we would conclude the surface of the Fe samples is C_s symmetry, which is the intersection of these two restriction.

One more important thing is that s-polarized output of SH intensity is almost zero. For C_s symmetry, SH intensity can be described as following. There are ten nonzero components of the nonlinear optical susceptibility tensor corresponding to C_s . Among them, χ_{xxx} , χ_{xyy} , χ_{zzz} , χ_{yyz} , and χ_{xxz} are components related with C_{2v} symmetry as described in Eq. (1). If these five components are predominant, s-polarized output should be very small compared to p-polarized one. Therefore it can be concluded that the surface of Fe film has C_s symmetry and also very close to C_{2v} .

$$\begin{pmatrix} P_x^{2\omega} \\ P_y^{2\omega} \\ P_z^{2\omega} \end{pmatrix} = \begin{pmatrix} \chi_{xxx} & \chi_{xyy} & \chi_{xzz} & 0 & \chi_{xxz} & 0 \\ 0 & 0 & 0 & \chi_{yyz} & 0 & \chi_{yxy} \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & 0 & \chi_{zxx} & 0 \end{pmatrix} E_j E_k \quad (1)$$

Cubic fcc and bcc (110) surface have many symmetry operators. For example, for the cubic fcc and bcc single crystal, the first atomic layer of fcc crystal has D_{2h} symmetry, bcc single crystal cannot have C_s symmetry. However, for the diamond structure single crystal, (110) surface has only C_s symmetry including operators 1, $\bar{2}_z$ without a vertical translation of one layer and C_{2v} as described in Ref 1. Even though the samples we measured are not single crystals but polycrystalline materials, it is expected that there is certain relation between the surface of polycrystalline Fe and C_s .

Fe films with various thickness are measured to find the

nonlinear optical susceptibility components representing C_s surface symmetry. We measured normalized SH asymmetry for sp configuration. We chose sp configuration for a convenience of susceptibility calculation because only one component χ_{xxx} contributes to SH intensity. The profile of the SH intensity for the sp configuration could be described $A + B\sin\phi$ form, where A corresponds to isotropic contribution to SHG and B reflects sinusoidal asymmetric contribution. Therefore we can define normalized SH asymmetry as the ratio of β_3/α_3 , where

$$\begin{aligned} A &= \alpha_1 + \alpha_2 I + \alpha_3 I^2 \\ B &= \beta_1 + \beta_2 I + \beta_3 I^2 \end{aligned} \quad (2)$$

To discriminate isotropic contribution $\alpha_3 I^2$ from dark current of measurement $\alpha_2 I$, SHG intensity has been measured with changing the incident power. Fig. 4 shows SH intensity breaks down due to high focused beam. Sample is damaged at 100 mW incident beam. SH intensity of Fe film no longer follows square law after damaged. Therefore experiments have been done only under 0~80 mW incident light.

Each rotational anisotropy measurement results in different SH intensity even though we measure SHG for the same sample. SH intensity critically depends on the distance between the film and the object lens. It is difficult to keep exactly same distance whenever we mount a sample on the holder. Therefore it is necessary to normalize SHG intensity B (more exactly $\beta_3 I^2$) with respect to into $\alpha_3 I^2$. Furthermore, we can eliminate unfiltered fundamental light, noise and stray light in laboratory efficiently by subtracting non-square term of Eq. (2).

$$I = I_{noise}(\omega) + A(2\omega) + B(2\omega) \sin\phi \quad (3)$$

Fig. 4. The dependence of SH intensity on increasing incident powers.

Fig. 5. The normalized SH asymmetry with increasing film thickness.

From normalized SH asymmetry β_3/α_3 , the symmetry class of the film can be precisely determined in C_s or C_{2v} . The change of β_3/α_3 with respect to the film thickness is depicted in Fig. 5. It should be noted that this asymmetry is originated from the structure of film surface because magnetization-induced SHG (MSHG) intensities show isotropic behavior, which are not included in this paper. Thin films have isotropic surface and SH asymmetry increases up to 300 nm with increasing thickness. It can be deduced that films are initially deposited in an isotropic way and film structure is gradually changed to bulk structure with increasing film thickness.

IV. Conclusion

In conclusion, we proved experimentally that polycrystalline Fe thin film on glass substrate showing (110)

growth orientation has crystal classes C_s or C_{2v} corresponding to (110) surface through symmetry consideration of nonlinear optical susceptibility tensor components. Fe film surfaces used in this paper have C_s symmetry very close to C_{2v} confirmed from rotational anisotropy measurement of SHG. Structural anisotropy of film is increased with increasing film thickness and saturated at 300 nm thickness. It can be deduced that isotropic thin films become more and more anisotropic with increasing thickness.

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