Phase transformation at interface using femtosecond laser irradiation†

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KEY WORDS : (Femtosecond laser) (Thin film) (Interface) (Phase transformation)

1. Introduction

Interfaces in solids indicate very small areas with nanometer scales such as grain boundaries between internal solids, and they usually decide or dominate the mechanical, thermal, and optical properties of the bulk material. Recently, high-resolution TEM provides much information about interfaces and reveals the mechanism of additives, mainly rare-earth elements, for an improvement of strength. The development of controlling the interface is one of the crucial subjects in material processing.

The femtosecond laser has been widely used in material processing because of its ability to suppress thermal damages and to form refractive index changes near the focal point. It is possible to fabricate and modify various nanostructures inside transparent materials using multiphoton absorption at the focus due to the extremely high-intensity of the laser pulses. It has previously been reported that refractive index changes at the focus inside glass was approximately 10^{-4} to 10^{-3}, depending on the laser irradiation condition. We have been developing laser processing to form sub-micro holes [1] and for defect control [2] using the laser. To utilize the increase of temperature and pressure in a very short time enables us to reform the ion distribution inside the glass. [3]

Here, we tried to control the phase transformation of Fe-Si thin film or interfaces between the film and a substrate using femtosecond laser irradiation. [4] In addition, silicon deposition at the interface was also demonstrated using the photo reaction between Al thin film and a glass substrate with the assistance of the laser pulses. The composition and the surface of the reacted area were evaluated using SEM, TEM, XRD, and confocal Raman spectroscopy.

2. Experimental procedure

Fe-Si amorphous thin film with a thickness >2μm was prepared using a radio-frequency (rf) sputtering method (ULVAC RFS-200). Fe (99.9%, Kojundo Chemistry) and Si (99.999%, Kojundo Chemistry) powders with a mole ratio of 1 : 2 were mixed using an alumina mortar for 30 minutes. Next, the mixture was compacted to use as a target for the rf sputtering. A non-dope silicon (100) single crystal or fused silica substrate with the dimensions of 10×10×1 mm^3 was mounted parallel to the target at a distance of 30 mm, and the thin amorphous Fe-Si film was deposited on each substrate under the following conditions : the RF power was 100W, the sputtering gas was 100% Ar, and the sputtering pressure was 30mTorr at room temperature. The thickness of the prepared film was evaluated using a surface roughness meter (KLA Tencor, P-15).

A regeneratively amplified mode-locked Ti:sapphire laser operating at a wavelength of 800nm (RegA 9000, Coherent), with a 120fs pulse width, 200 ～ 250kHz repetition rate was used as a light source in this experiment. The fabricated Fe-Si thin film sample was fixed on an *x-y-z* stepping motor stage and the laser beam with a diameter of ~3mm was focused on the film in air through a 10× objective lens with a numerical aperture of 0.3. We confirmed that oxidation did not occur in the laser irradiation in air from XRD analysis. The pulse energy at the sample location was precisely controlled using a neutral density filter between 0.25 and 1.5 μJ. The sample was scanned at different speeds (250-600μm/sec) along a horizontal direction, perpendicular to the incident laser beam, and the scanning process was repeated many times to form a square photomodified area with the dimensions of 10×10 mm^2 in order to carry out the various analysis described below. The chemical composition of the photomodified area was analyzed using X-ray diffraction (XRD) under CuKa radiation (Rigaku RINT2500) in order to verify the phase transformation in the film. The

† Received on 30 September 2010

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Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

microstructure of the photomodified surface area was observed using a scanning electron microscope (SEM : Hitachi S2600N). The atomic distribution at the photomodified area was also analyzed using electron probe micro analysis (EPMA, JEOL, JSM-8000).

3. Results and discussions

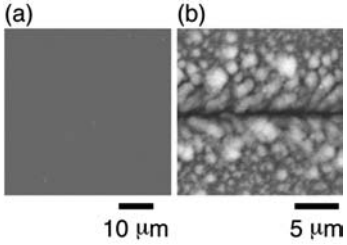

Fig.1. SEM photos of Fe-Si thin film before (a) and after (b) the laser irradiation.

Figure 1 shows SEM photographs of the surface of Fe–Si thin film before (a) and after (b) the femtosecond laser irradiation with a pulse energy of 1.5μJ. The Fe-Si compound has a band gap of ~ 0.85eV and high optical absorption, therefore, the film would sufficiently absorb the incident laser beam. When the laser pulses were focused on the film, the focal spot of the laser beam was illuminated, and a dispersion of white particles less than ~3μm in diameter was observed around the scanning area as indicated in this photo.

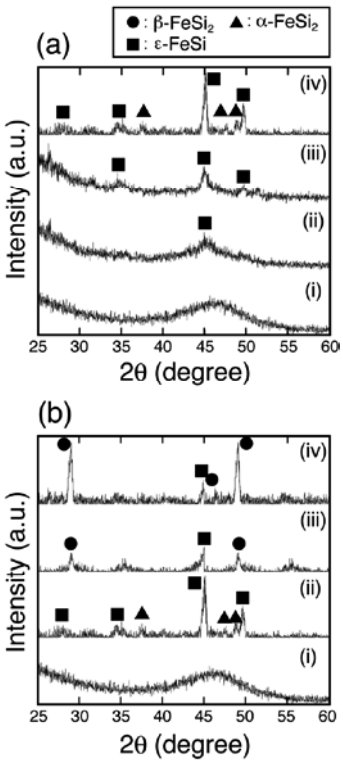

Fig. 2. (a)XRD patterns of the Fe-Si thin film after the laser irradiation with different pulse energy;(i)as-deposited, (ii)0.25μJ, (iii)0.75μJ, and (iv)1.5μJ, respectively. (b) XRD patterns of the film after the laser irradiation at different scanning speeds;(i)as-deposited, (ii)250μm/sec., (iii)450μm/sec., and (iv)600μm/sec., respectively.

Figure 2(a) indicates XRD patterns of the Fe-Si thin film (i)as-deposited, and after the laser exposure with a different pulse energy of (ii) 0.25μJ, (iii) 0.75μJ, and (iv)1.5μJ, respectively.The scanning speed of the sample was set to 250μm/sec. The exposed area was apparently crystallized and two phases ascribed to α-$FeSi_2$ and ε -FeSi phases were identified in the XRD spectra. In addition, the crystallinity of these phases improved as the pulse energy of the laser pulses increased, especially in the case of 1.5μJ. The white particles shown in Fig. 1(b) were due to the crystalline Fe_xSi_y compounds formed by the laser irradiation. In the phase diagram of a Fe-Si binary system, stoichiometric β-$FeSi_2$ is composed of 68at.% Fe and 32at.% Si. The β-$FeSi_2$ phase easily transforms into α–$FeSi_2$ and ε -FeSi phases by heat treatment at over 1255K. We confirmed that our amorphous thin film transformed into β-$FeSi_2$ phase by heat treatment at 1123K for 6 hours, and the mixture of α- $FeSi_2$ and ε -FeSi at 1373K. In Fig. 2(a), no peaks corresponding to the β-$FeSi_2$ phase existed, presumably due to the decomposition of β-$FeSi_2$ during the excess laser exposure.

Fig. 2(b) shows XRD patterns of the Fe-Si thin film before (i) and after the laser irradiation with different scanning speeds of (ii)250μm/sec., (iii)450μm/sec., and (iv)600μm/sec., respectively. The pulse energy of the laser beam was set to 1.5μJ in all cases. When the scanning speed was set to 250μm/sec., both the α-$FeSi_2$ and ε -FeSi phases were observed at the photomodified area. However, when the scanning speed increased to above 450μm/sec., their peak intensity decreased and the β-$FeSi_2$ phase appeared instead. The fast laser scanning at above 600μm/sec. could form almost the single β-$FeSi_2$ polycrystalline phase. Therefore, the phase transformation strongly depends on the scanning speed and pulse energy in the Fe-Si system.

The initial temperature at the focus is important for the ultrafast crystallization using the laser pulses. The scanning speed is one of the important parameters in the crystallization of Fe-Si thin films to control cooling or heating rate around the focus. In general, when the femtosecond laser beam is focused inside solids, not only the generation of shock wave but also heat accumulation occurs around the focal point, resulting in the formation of ion diffusion or refractive index change with a circular shape after the laser irradiation. The effect depends on the temperature cooling rate: if the cooling rate is low, the effect tends to occur around the focal area. We have calculated the cooling rate near the focal point in the case of the laser irradiation on $FeSi_2$ thin film by solving the thermal diffusion equation. The rate is calculated to ~10^{12} K/s, which is much faster than that of the commercial glass sample (~ 10^8 K/s), due to its large thermal diffusivity ($D_{th:FeSi}$ = 0.65) rather than that of glass sample ($D_{th:glass}$= 0.46×10^{-6}). Therefore, we can estimate that the focal temperature increases dramatically and relaxes to room temperature before the next pulse arrives. The phase transformation completed in a very short time before the heat accumulated.

4. Conclusion

Phase transformation in amorphous Fe-Si film was demonstrated using femtosecond laser irradiation. The formation of α-$FeSi_2$, β-$FeSi_2$ and ε -FeSi depended on

the focal energy from the laser : the moderate irradiation tends to form the β-$FeSi_2$ phase. To control the photon energy will open up the various photo-reactions at the interface.

5. References

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