Amorphization Induced by Focused Ion Beam Milling in Metallic and Electronic Materials

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Abstract: Focused ion beam (FIB) milling using high-energy gallium ions is widely used in the preparation of specimens for transmission electron microscopy (TEM). However, the energetic ion beam induces amorphization on the edge of specimens during milling, resulting in a mischievous influence on the clearness of high-quality transmission electron micrographs. In this work, the amorphization induced by the FIB milling was investigated by TEM for three kinds of materials, metallic materials in bulk shape, and semiconductive and electronic ceramic materials as a substrate for the deposition of thin films.

Key words: focused ion beam (FIB), transmission electron microscopy (TEM), amorphization, metallic, semiconductive, electronic ceramic materials

INTRODUCTION

There are several methods to prepare specimens for transmission electron microscopic (TEM) analysis. Focused ion beam (FIB) milling using energetic Ga ions is widely employed in the TEM specimen preparation (Yabuuchi et al., 2004; Rubanov & Munroe, 2005), as this method makes it possible to thin a selected specific micro-area of crude samples more rapidly. There are some advantages in using FIB for TEM specimen fabrication: (1) complex heterogeneous structures with different sputtering rates can be thinned uniformly, (2) wide thin areas of uniform thickness can be prepared, and (3) specific regions of interest can be located with precise accuracy for cross-section fabrication (Yu et al., 2006). However, the high-energy Ga ion beam that is used to section materials also creates artifacts in the specimen (Cairney & Munroe, 2003; Prenitzer et al., 2003; Rubanov & Munroe, 2005). These artifacts include the implantation of Ga atoms, the generation of amorphous regions, the introduction of point defects and dislocations, and also the redeposition of milled material onto the faces of the thinned materials (Cairney & Munroe, 2003; Prenitzer et al., 2003), which can have a mischievous effect on the high-quality TEM. Among them, milling-induced amorphization is due to the irradiation of ions onto the surface of the material, where the reaction of the ions with the materials atoms can destroy the crystalline structure (Baba et al., 1997).

Numerous studies have been conducted on FIB damages. Most of them have been carried out on the influences of the accelerating voltages, the beam current, or the incident angle of ion beam on the FIB-induced damages with a couple of specific materials of a same kind, such as elemental semiconductive materials (Si and Ge; Kato, 2004; Wang et al., 2005), III–V compound semiconductive materials (Yabuuchi et al., 2004; Rubanov & Munroe, 2005), or metal-

lic materials (Yu et al., 2006). Here, we report the comparison of amorphized region induced by FIB milling for three kinds of materials, which are widely used as academic and industrial engineering materials, metallic materials in bulk shape, and semiconductive and electronic ceramic materials as a substrate for the thin film deposition.

MATERIALS AND METHODS

For this study, the Fe, Cu, Mo, and Ni of polycrystalline were thinned with FIB milling as metallic materials in bulk shape. The samples employed for FIB milling were (001) Si and (001) GaAs as semiconductive materials, and SrTiO₃ (STO) and α -Al₂O₃ (sapphire) as electronic ceramic materials, all of which were single crystal. The semiconductive and electronic ceramic material samples were mounted in an FIB system with their surface normal to the ion beam.

All the samples were thinned by FIB using Ga ions on a SII SMI3050SE [FIB/SEM (scanning electron microscope) dual-beam hybrid system]. Of various FIB-TEM specimen preparation techniques, the “lift-out” technique combined with the “H-bar” technique was used for TEM specimen milling (Li et al., 2006). An identical milling condition with the accelerating voltage of 30 kV, the beam current of 95 pA, and the FIB incidence angle of $\pm 1.3^\circ$ was applied to all the samples in this experiment. This FIB milling condition has been widely used for a rapid and suitable TEM specimen preparation with a minimum damage to target materials (Kato, 2004; Yu et al., 2006).

As shown in Figure 1a, every sample was fabricated by FIB as a TEM specimen with the shape of wedge. Figure 1b is an SEM image of the wedge-type milled specimen, acquired by the FIB/SEM dual-beam hybrid system. A damage-expected region due to amorphization is indicated in the thinner zone of the wedge.

The amorphization in each specimen was examined in a JEOL JEM-2100F TEM (point resolution: 0.19 nm) at an

Figure 1. **a:** A schematic diagram of transmission electron microscopy specimen fabrication by focused ion beam. **b:** A scanning electron microscopy image of the wedge-type milled specimen.

accelerating voltage of 200 kV, equipped with an energy-dispersive X-ray (EDX) detector (Oxford Instruments INCA). Bright-field and high-resolution TEM images and selected area electron diffraction patterns were obtained for the evaluation of thickness and crystallinity of the amorphized layer generated by FIB. The thickness of amorphous layers was defined and measured as the distance from the edge of specimen to the boundary between crystalline structure and amorphized region with the direction of electron beam parallel to crystal planes using electron diffraction patterns. For the elemental identification, EDX spectra were acquired from the specimens.

RESULTS AND DISCUSSION

Figure 2 is TEM results after FIB milling of metallic material samples. In the four metallic materials, bright-field TEM (BF-TEM) images (Figs. 2a, 2c, 2e, 2g) show the edge of each FIB-milled specimen, and electron diffractions and EDX spectra were insetted on the BF-TEM images. The electron diffractions and the magnified high-resolution TEM (HRTEM) images (Figs. 2b, 2d, 2f, 2h) were acquired from the dotted parts on the BF images, respectively.

As known from the clear HRTEM images and the electron diffractions, the crystallinity was even retained to the end of edge in the four metallic material specimens after FIB milling with the maximum accelerating voltage of 30 kV. FIB-induced amorphization was negligible in the metallic materials, as their crystallinity is almost never affected over the entire area by FIB milling.

Figures 3a and 4a are BF-TEM images of FIB-milled semiconductive materials (Si and GaAs), showing that an amorphized layer with the average thicknesses of 237 ± 23 nm in Si and of 99 ± 7 nm in GaAs was generated by FIB on the edge region, respectively. Below the FIB-amorphized layer in both materials, there is a layer where it looks like the coexistence of amorphous state and crystalline state. The coexistence-looking layer is just a consequence of the transition of relative thickness of the surface amorphous layer to that of crystalline interior, not indicating a transition of structure from crystalline to amorphous phases. Figures 3b–3d and 4b–4d are the HRTEM images magnified

Figure 2. Transmission electron microscopy results after focused ion beam milling of metallic material samples, Fe (**a,b**), Cu (**c,d**), Mo (**e,f**), and Ni (**g,h**).

from the dotted parts on the BF-TEM images of Figures 3a and 4a, with the insets of electron diffractions showing their crystallinity state. The HRTEM images and electron diffractions make sure of the progress of amorphization by FIB on the edge of the both materials.

Figures 5 and 6 are TEM results of the edge in STO and sapphire, as electronic ceramic materials, after FIB milling. An amorphized layer induced by FIB was generated with the average thicknesses of 11.6 ± 0.3 nm in STO and of 15.2 ± 1.6 nm in sapphire, respectively. A relative transition region looking like the mixture of amorphous state with crystalline state does not exist in contrast to the case of Si and GaAs. The dotted parts of Figures 5a and 6a were magnified to the HRTEM images of Figures 5b and 6b.

Figure 3. a: A bright-field transmission electron microscopy image and (b–d) high-resolution transmission electron microscopy images magnified from the dotted parts on (a) with the insets of electron diffractions of the focused ion beam-milled Si specimen.

Figure 4. a: A bright-field transmission electron microscopy image and (b–d) high-resolution transmission electron microscopy images magnified from the dotted parts on (a) with the insets of electron diffractions of the focused ion beam-milled GaAs specimen.

After FIB milling, the crystallinity has been retained to the end of edge without the damage by FIB in the metallic materials such as Fe, Cu, Mo, and Ni, while an edge with the thickness of about 11–17 nm has been amorphized without a relatively amorphized transition layer in the electronic ceramic materials. In the case of the semiconductive materi-

Figure 5. Transmission electron microscopy results of the edge in SrTiO_3 after focused ion beam milling.

Figure 6. Transmission electron microscopy results of the edge in sapphire after focused ion beam milling.

als, an amorphized layer with a comparatively high thickness including a relative transition region was generated by the collision of accelerated Ga ions in comparison with the other two kinds of materials. Therefore, under the condition of FIB milling in our experiment, which is widely used for the efficient TEM specimen preparation with FIB (Kato, 2004; Yu et al., 2006), the crystallinity is almost never affected in metallic materials; on the other hand, it is most affected in semiconductive materials.

It can be remarked that both semiconductive materials of Si and GaAs have a considerable difference of the thickness of an amorphized layer, which results from the extent of atomic mixing by recoil implantation due to sputter yields of both materials. The sputter rate for III–V compounds is much higher than for Si and Ge (Rubanov & Munroe, 2005). The sputter rate of GaAs is determined to be about six times greater than in Si. The higher sputter rate with efficient energy in sputtering atoms in target materials can bring about the minimal effect of atomic mixing leading to the reduction of amorphization thickness. During FIB milling, accelerated Ga ions collide with the target material atoms and displace them. If the surface binding energy is high, then fewer atoms can release from the target materials. Unlike elemental semiconductive materials (Si), the surface binding energy for III–V semiconductive materials is slightly different for each species in the compound. Of course, other factors, such as melting point, may also affect the rate at which materials are sputtered during milling (Prenitzer et al., 2003; Rubanov & Munroe, 2005). In

Table 1. Elemental Quantification from the Energy-Dispersive X-Ray Spectrometer (EDS) Data Acquired from the Focused Ion Beam (FIB)-Milled Materials.

Materials	Quantified Atomic Fractions
Fe	Fe (98.7%), C (0.36%), Ga (0.94%)
Cu	Cu (99.8%), Ga (0.17%)
Mo	Mo (99.6%), Ga (0.38%)
Ni	Ni (99.6%), Ga (0.37%)
Si	Si (99.2%), Ga (0.76%)
GaAs	Ga (49.9%), As (50.1%)
STO	Sr (21.6%), Ti (22.3%), O (55.6%), Ga (0.51%)
Sapphire	Al (41.8%), O (57.8%), Ga (0.45%)

addition, the effect of ion implantation by energetic Ga ions should be considered. It has been shown that averaged atomic fraction of Ga for all the samples except GaAs is about 0.51%, as the result of elemental quantification from our energy-dispersive X-ray spectrometer (EDS) data in Table 1. Because it is known that the atomic fraction <5% is meaningless in the EDS analysis, the effect of ion implantation can be neglected in our study. And the EDS quantification result has demonstrated that stoichiometric composition has been retained in the compound materials in spite of the amorphization by ion collision.

The damaged structures induced by FIB milling differ in different materials such as metallic, semiconductive, and other materials. The differences arise from the differing defect mobility and recovery behavior of each material (Sugiyama & Sigasato, 2004) and the sputter yield determined by the mass ratio between incident ion and target atoms. The sputter yield is also affected by the binding energy of target atoms, which is in turn related to the heat of sublimation or melting point. Even though an identical material is thinned by FIB, the damaged structure may be different depending on FIB milling conditions such as accelerating voltage, beam current, thinning area, milling time, incident angle, specimen temperature, or grain size (Kato, 2004; Yabuuchi et al., 2004; Wang et al., 2005). In our study, the amorphization of three kinds of materials, metallic, semiconductive, and electronic ceramic materials, was compared after FIB milling using the H-bar and lift-out technique under the widely used milling condition. There is no problem against the preparation of specimen using FIB for TEM observation of metallic materials in a bulk shape under this milling condition. As the amorphization of specimen edge is unavoidable in the FIB preparation of the electronic materials on which thin films are deposited, there should be methods to avoid or reduce the amorphization. The amorphized damage can be minimized by coating a protective layer of carbon, gold, palladium, or platinum, the electron beam deposition of metal film, and the formation of a plasma-polymerized organic film on the sample surface before FIB milling (Wang et al., 2005). In particular, the thickness of an amorphized layer in semiconductive materials is very high, and therefore it may be recommended to polish the specimens by the soft milling with the ion beam

of low-energy, low-current, and small incidence angle at the final milling step (Wang et al., 2005), to use a reactive gas during FIB milling (gas-assisted etching; Sugimoto et al., 1990), and to etch with broad Ar ion beam after FIB milling (Yabuuchi et al., 2004), for much higher quality of TEM images.

CONCLUSIONS

Three kinds of materials, the metallic materials in a bulk shape (Fe, Co, Mo, and Ni), the semiconductive materials (Si and GaAs), and electronic ceramic materials (STO and sapphire), which are used as a substrate for thin film deposition, were thinned under the identical milling condition with FIB for TEM specimens. Amorphization of an edge in the specimens was investigated with TEM for the comparison. The metallic materials did not have an FIB-induced amorphous layer on the edge, although amorphization occurred in the electronic materials (semiconductive and electronic ceramic) during FIB milling. In particular, the semiconductive materials had higher thickness of an amorphized layer than the electronic ceramic materials. The methods to prevent TEM specimens from being amorphized during FIB milling should be required for high-quality TEM.

ACKNOWLEDGMENTS

The authors thank Mr. Ki Hwan Kim and Mr. Jae Deok Kim for sample preparation in this study. This work was supported by Project Code 2009H013 from RIST and Project code 2011D003 from the Ministry of Knowledge Economy in Republic of Korea.

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