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# Density Measurement of Thin Films by X-ray Reflectivity Spectra

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Density of several Sb-based phase-change optical recording thin films is estimated by X-ray reflectivity measurements. These films with 100 nm thick are formed by magnetron sputtering on glass substrates. The films are amorphous phase except for Sb as the deposited state. Crystalline films are prepared by LASER annealing of the corresponding amorphous films. Reflectivity is measured for both the amorphous and crystalline films of several Sb-based compositions with the X-ray of photon energy 5keV at BL03 at SR center of Ritsumeikan University. Density, thickness and surface/interface roughness are determined so as to make Parratt's simulation curve fit the observed reflectivity curve. There is little difference in density between amorphous and crystalline phases for the same composition film. Densities are estimated at 6.4(6.6), 6.5(6.7), 6.6(6.8) and 6.7(7.0) g/cm$^3$, for Ga-Sb, Sb, Sb-Te and In-Sb, respectively, where the figures in parentheses are calculated values for crystalline films according to the unit-cell volume from the X-ray diffraction data. Parratt's simulation also indicates that some oxide thin layer with 2-6 nm is formed on the surface of crystalline phases.
Key words: X-ray reflectivity, thin films, density, Sb-Te, alloy

## 1. INTRODUCTION

The quarternary alloy system AgInSbTe was first reported in 1991 as completely erasable phase-change materials[1]. Since then, this material is widely used as recording material in phase-change media such as CD-RW and DVD+RW[2]. By these days, 1 to 4x DVD media with AgInSbTe-system have been developed. It is easy to get higher data transfer rate media using this material because the crystallization speed of AgInSbTe could rise by increasing the Sb concentration. However the higher Sb concentration becomes, the worse thermal stability of amorphous marks becomes. To achieve further high-speed media, several Sb-based binary phase-change materials are investigated.

Density of thin films is hard to measure without use of X-ray reflectivity. Some differences such as in the magnitude of the K-edge-jump of Sb[3] or photoelectron-yield[4] between the amorphous and crystalline films, suggest that the density of the amorphous film is little greater than that of the corresponding crystalline one. Is there any volume change involved in the amorphous/crystalline phase-change? Does the density for several compositions of crystalline films agree with the calculated density from the unit-cell volume measured by X-ray diffraction on the corresponding crystalline films?

## 2. EXPERIMENTAL

### 2.1 X-ray reflectivity

Films with 100 nm thick of the several Sb-based binary alloys are deposited on glass substrates by magnetron sputtering. Reflectivity was measured by use of the goniometer at BL03 at Ritsumeikan SR-center. This goniometer is installed in a vacuum chamber and enables us to measure from 3 to 8 keV of photon energy. This beamline is for X-ray reflectivity measurement combined with a total reflection X-ray fluorescence detection system and enables us to perform XAFS measurement of both reflection and fluorescence modes. A shielded proportional counter is used as a detector for reflected X-ray and Xenon is used as charged gas (250 Torr) in this counter to obtain high-counting efficiency in the high X-ray energy range. The counter has low background (40cpm) and high-counting rate up to several hundreds of thousands of cps. The dynamic range of reflection curve is estimated to be 6 orders of magnitude. Nickel foils with no/10/20/40 μm thick are selectable as an attenuator according to the reflected beam intensity. The incident X-ray is monitored by a 50 mm-long ionization chamber filled with nitrogen gas.

### 2.2 X-ray diffraction

Powder X-ray diffraction is able to measure only for crystalline samples. Powder samples, which are collected from the crystalline films (15 nm thick) of several alloy compositions are packed into quartz capillary tubes with an internal diameter of 0.2 mm. The measurement was carried out with a large-diameter Debye-Scherrer camera at SPring-8[5]. The wavelength of X-ray beam is 0.0419 nm.

## 3. RESULTS AND DISCUSSION

### 3.1 X-ray reflectivity

Recorded reflectivity spectra are shown in Fig. 1(a) for amorphous films; a-GaSb, a-SbTe, a-InSb and in Fig. 1(b) for crystalline films; c-GaSb, c-SbTe, c-InSb, c-Sb, where the simulation curves (denoted by —— ) are also superposed upon the experiment curves ( denoted by ∘∘∘∘ ). The calculated values of density, thickness and

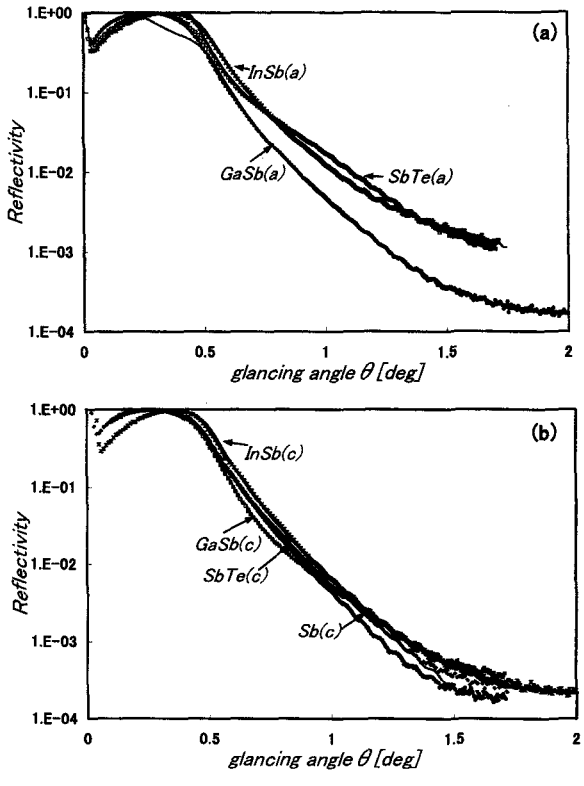


Fig.1(a),(b) Reflectivity of Sb-based alloy films.

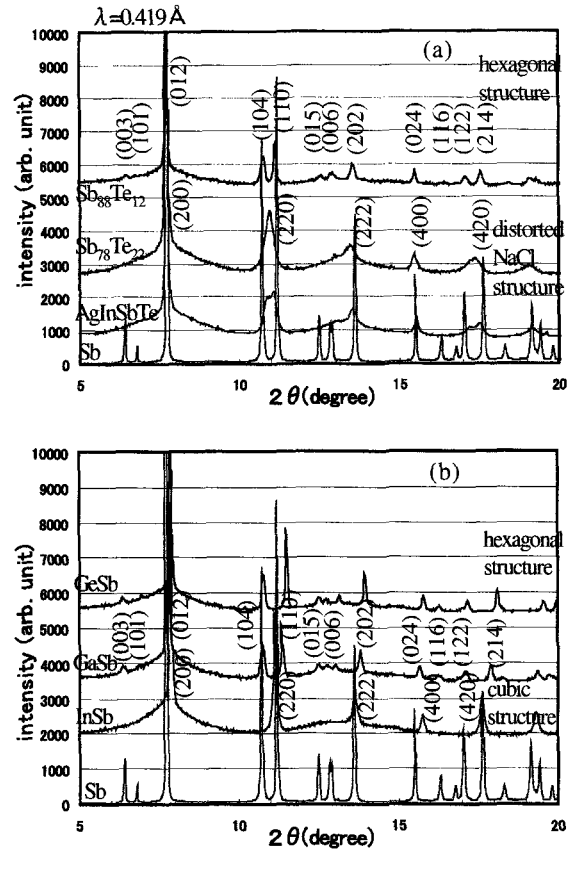


Fig.2(a),(b) X-ray diffraction of Sb-based alloys.

Table I Parameters calculated from X-ray reflectivity

| | (Amorphous) | | | (Crystalline) | | | |
|---|---|---|---|---|---|---|---|
| | Density [g/cm$^3$] | Thickness [nm] | Roughness [nm] | Density [g/cm$^3$] | Thickness [nm] | Roughness [nm] | |
| Sb | No data | | | — | — | — | 2nd layer |
| | | | | 6.5 | 98.8 | 1.5 | 1st layer |
| | | | | 5.0 | ∞ | 0 | Substrate |
| Ga12Sb88 | — | — | — | 6.1 | 2.0 | 1.3 | 2nd layer |
| | 6.3 | 97.0 | 1.1 | 6.4 | 89.1 | 0.3 | 1st layer |
| | 4.0 | ∞ | 0 | 4.0 | ∞ | 0 | Substrate |
| Sb78Te22 | 6.1 | 7.8 | 0.6 | 6.1 | 6.4 | 1.3 | 2nd layer |
| | 6.6 | 86.4 | 0.6 | 6.6 | 89.4 | 0.5 | 1st layer |
| | 4.0 | ∞ | 0 | 4.0 | ∞ | 0 | Substrate |
| In31.7Sb68.3 | — | — | — | — | — | — | 2nd layer |
| | 6.5 | 94.0 | 1.1 | 6.7 | 93.0 | 1.3 | 1st layer |
| | 4.0 | ∞ | 0 | 4.0 | ∞ | 0 | Substrate |

surface/interface roughness are listed in Table I. Substrate density is calculated little higher owing to the reduced dynamic range of measurements. The *R*-factors are estimated at 0.54-0.85% for the least square curve-fitting region of 0.5-1.6 deg.

3.2 X-ray diffraction

Powder X-ray diffraction patterns of Sb-based alloys are shown in Fig. 2(a); SbTe, AgInSbTe and Sb, in Fig. 2(b); GeSb, GaSb, InSb and Sb. These alloys are all crystalline and the lattice constants are determined from the corresponding diffraction patterns. The lattice constants, unit-cell volume, number of atoms in the unit-cell, averaged atomic weight and calculated density are shown in Table II. All the lattices here are adapted for the hexagonal system.

3.3 Conclusions

The obtained density by X-ray reflectivity is consistent with the density calculated from X-ray diffraction. The Sb-based alloys are arranged InSb>SbTe>Sb>GaSb in order of high density[6]. The density difference between the amorphous and crystalline films for the same composition is less than the errors of analysis and

Table II Theoretical density calculated from X-ray diffraction for crystalline samples

| | (Crystalline) | | | | | |
|---|---|---|---|---|---|---|
| | *a*[Å] | *c*[Å] | V[Å$^3$] | Z | Averaged atomic mass | Theoretical density |
| Sb | 4.30 | 11.27 | 180.51 | 6 | 121.75 | 6.7 |
| Ga12Sb88 | 4.24 | 11.30 | 176.04 | 6 | 115.51 | 6.6 |
| Sb78Te22 | 4.40 | 10.77 | 180.67 | 6 | 122.99 | 6.8 |
| In31.7Sb68.3 | 4.32 | 10.62 | 171.85 | 6 | 119.55 | 7.0 |

experiments. Then the reported difference in the magnitude of the Sb K-edge-jump between amorphous and crystalline films was occurred owing to the film thickness change by evaporation. The samples concerned in this study are considered to be no evaporation occurred because of the low power LASER annealing. The difference of magnitude of photoelectron-yield between the amorphous and crystalline films is considered as the effect of electronic transition mechanism, not as the density effect. Analyzing X-ray reflectivity one can see that some thin layer with 2-6 nm is coated on the surface especially for crystalline phase samples. Probably, this layer is made of some oxide and was formed during LASER annealing.

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