Initial growth of Se$_{100-x}$Te$_x$ alloy films deposited on Au(111) surfaces

Seiichi Nagashima

College of Engineering, Nihon University, Koriyama-shi, Fukushima-ken 963-8642, Japan

E-mail: nagasima@ge.ce.nihon-u.ac.jp

Abstract. The initial growth processes and surface structures of Se$_{100-x}$Te$_x$ alloy (where $x = 0, 30, 50, 80$ and $100$ at. %) thin films deposited on Au(111) surfaces at $298 \text{K}$ have been studied by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). Experimental results of AES were analyzed by analytical model [Appl. Surf. Sci. 240 (2005) 189]. AES results predict that after one monolayer (1ML) of Se thin film is completed in layer-by-layer growth, island growth begins. For Se$_{70}$Te$_{30}$ film, after 1ML is completed in layer-by-layer growth, simultaneous multilayer (SM) growth begins. For Se$_{50}$Te$_{50}$ film, after 1ML is completed in SM growth, island growth begins. For Se$_{20}$Te$_{80}$ and Te films, these films grow in island growth. On the other hand, LEED results show that at coverage of 1ML, Se, Se$_{70}$Te$_{30}$ and Se$_{50}$Te$_{50}$ films show the $\sqrt{3} \times \sqrt{3}$R30$^\circ$ structure. With increasing coverage, these films transform to the reconstructed $(1 \times \sqrt{7})$R79.1$^\circ$ surface which is observed up to about 3ML. Se$_{20}$Te$_{80}$ and Te films show incommensurate (31$^\circ$R30$^\circ$) structure at coverage of 1ML. For further deposition, a reconstructed surface is not observed in the Se$_{20}$Te$_{80}$ film, but in the case of Te film, $(3 \times 3)$ and complex structures are observed.

1. Introduction

The chalcogenides based on Se and Te are well-known and promising materials for variety of photonic applications. Most works have concentrated on the various photoelectric properties of amorphous Se$_{100-x}$Te$_x$ alloys [1]. A few papers have dealt with the epitaxial growth of crystalline Se$_{100-x}$Te$_x$ alloys [2]. However, little attention has been paid to the initial growth processes of Se$_{100-x}$Te$_x$ alloy films deposited on Au(111) surfaces. Moreover, it is not known whether initial growth processes of Se$_{100-x}$Te$_x$ alloy films deposited on Au(111) surfaces change by composition $x$. The purpose of the present study is to clarify this question. In order to study the effect of Te content on the growth processes of Se$_{100-x}$Te$_x$ alloy films, the specimen with various $x$ (0, 30, 50, 80, 100 at. %) were prepared. The experimental and theoretical results of AES performed during the growth of Se$_{100-x}$Te$_x$ alloy films on Au(111) surfaces will show that when the composition $x$ increases, the growth of Se$_{100-x}$Te$_x$ alloy films of one monolayer (1ML) is shifted from layer-like growth towards island-like growth. Furthermore, the epitaxial relationship between Se$_{100-x}$Te$_x$ alloy films and Au(111) surfaces is reported.

2. Experimental

A clean Au(111) single crystal surface used as a substrate was prepared by vapor deposition in an ultrahigh vacuum chamber (base pressure $8 \times 10^{-8} \text{Pa}$). Details have been described elsewhere [3]. Au of 99.99% purity was evaporated from a conical tungsten filament source, and deposited on
air\-cleaved MoS$_2$ substrate at 590±2 K. A typical thickness of Au film was 100 nm. Se$_{100-x}$Te$_x$ alloys with the composition of x = 0 (pure Se), 30, 50, 80 and 100 (pure Te) at. % were deposited in short intervals onto Au(111) surfaces at 298±2 K from a conical tungsten filament source which was mounted inside a water cooled shroud. Deposition time of Se$_{100-x}$Te$_x$ alloys was controlled by a microcomputer\-aided shutter, and the film thickness of Se$_{100-x}$Te$_x$ overlayer was estimated from the deposition time. The surface structure and overlayer growth were examined \textit{insitu} by LEED and AES, respectively.

3. Results

**Se films.** Fig. 1a shows the intensity variations of Auger signals of Au (69 eV) and Se (99 eV) as a function of film thickness of Se overlayer. The intensity of Au Auger signal decreases drastically with increasing film thickness of Se up to 0.11 nm. For further deposition, Au Auger intensity increases slightly and the Auger intensity decreases again toward lower intensity at thickness above 0.14 nm. When the film thickness exceeds about 0.6 nm, the decrease of Au Auger intensity is very slow. Also, Se Auger intensity increases monotonously and slowly. In Fig. 1a, the solid and dashed lines represent theoretical results, which are based on layer\-by\-layer growth and island growth, respectively, to be discussed later. On the other hand, LEED results show that weak and broad extra LEED spots indicating (1 $\sqrt{3}$ $\times$ $\sqrt{3}$)R30$^\circ$ structure are observed up to 0.14 nm. When the film thickness exceeds about 0.6 nm, the Auger intensity decreases again toward lower intensity. Also, Se Auger intensity increases monotonously and slowly. In Fig. 1b, the solid and dashed lines represent theoretical results, which are based on layer\-by\-layer growth and island growth, respectively, to be discussed later. On the other hand, LEED results show that weak and broad extra LEED spots indicating (1 $\sqrt{3}$ $\times$ $\sqrt{3}$)R30$^\circ$ structure are observed at 0.11 nm. For further deposition, Au(111) - (1 $\times$ $\sqrt{7}$)R79.1$^\circ$ - Se structure is observed up to 0.4 nm. When the film thickness exceeds about 0.4 nm, the reconstructed structure is not observed.

**Se$_{70}$Te$_{30}$ alloy films.** Fig. 1b shows the variations of the Au (69 eV) and Te (483 eV) Auger intensities of Se$_{70}$Te$_{30}$ alloy films. The variation of Au Auger intensity is roughly similar to that of Se films. Also, Te Auger intensity increases monotonously with increasing film thickness. In Fig. 1b, the solid and dashed lines represent theoretical results to be discussed later. On the other hand, LEED results show that (1 $\sqrt{3}$ $\times$ $\sqrt{3}$)R30$^\circ$ structure is observed from 0.07 nm to 0.14 nm, and the sharpest extra LEED spots indicating (1 $\sqrt{7}$ $\times$ $\sqrt{7}$)R30$^\circ$ structure are observed at 0.11 nm. For further deposition, weak and broad extra LEED spots indicating (1 $\times$ $\sqrt{7}$)R79.1$^\circ$ - Se structure is observed up to 0.4 nm. When the film thickness exceeds about 0.4 nm, the reconstructed structure is not observed.

**Se$_{50}$Te$_{50}$ alloy films.** Fig. 1c shows the variations of the Au (69 eV) and Te (483 eV) Auger intensities of Se$_{50}$Te$_{50}$ alloy films. The intensity of Au Auger signal decreases with increasing film thickness. However, in the range of 0.1 nm - 0.4 nm, the decrease of Au Auger intensity is slower. When the film thickness of Se$_{50}$Te$_{50}$ alloy exceeds about 0.4 nm, the Auger intensity decreases again toward lower intensity. Also, Te Auger intensity increases monotonously and slowly with increasing film thickness. In Fig. 1c, the dashed lines represent theoretical results, which are based on SM growth, to be discussed later. On the other hand, weak LEED spots indicating (1 $\sqrt{3}$ $\times$ $\sqrt{3}$)R30$^\circ$ structure are observed from 0.06 to 0.12 nm. For further deposition, broad LEED spots indicating (1 $\times$ $\sqrt{7}$)R79.1$^\circ$ structure are observed up to about 0.4 nm, and the reconstructed structure is not observed at film thickness above 0.4 nm.

**Se$_{20}$Te$_{80}$ alloy films.** Fig. 1d shows the variations of the Au (69 eV) and Te (483 eV) Auger intensities of Se$_{20}$Te$_{80}$ alloy films. The intensity of Au Auger signal decreases monotonously with increasing film thickness, whereas Te Auger intensity increases monotonously with increasing film thickness. In Fig. 1d, the dashed lines represent theoretical results, which are based on island growth, to be discussed later. On the other hand, LEED patterns with satellite spots are observed from 0.06 to 0.12 nm, and these LEED patterns show the incommensurate (1 $\sqrt{3}$ $\times$ $\sqrt{3}$)R30$^\circ$ structure. For further deposition above 0.12 nm, the reconstructed structure is not observed.

**Te films.** Fig. 1e shows the variations of the Au (69 eV) and Te (483 eV) Auger intensities of Te films. The intensity of Au Auger signal decreases with increasing film thickness of Te up to 0.15 nm. However, Au Auger intensity increases slightly for further Te deposition. When
Figure 1. Auger signal intensity - film thickness function for Se$_{100-x}$Te$_x$ alloy films deposited on Au(111); (a) Se, (b) Se$_{70}$Te$_{30}$, (c) Se$_{50}$Te$_{50}$, (d) Se$_{20}$Te$_{80}$ and (e) Te. A mark ⬠ represents Auger intensity from Au substrate, and □ Auger intensity from Se$_{100-x}$Te$_x$ overlayer. The solid and dashed lines represent the calculated Auger intensity assuming different growth processes.

the film thickness of Te exceeds about 0.2 nm, the Auger intensity decreases again toward lower intensity. Also, Te Auger intensity increases monotonously with increasing film thickness. In Fig. 1e, the dashed lines represent theoretical results, which are based on island growth. On the other hand, LEED patterns with satellite spots show that the incommensurate $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure is formed at film thicknesses from 0.07 to 0.16 nm. For further deposition, the $(3 \times 3)$ structure is observed from 0.17 to 0.20 nm, and the complex LEED pattern is observed up to about 0.4 nm. The reconstructed structure is not observed at film thickness above 0.4 nm.

4. Discussion
We will estimate here the initial growth processes of Se$_{100-x}$Te$_x$ alloy films on the basis of model I proposed by Fu and Wagner for the determination of thin film growth mode [4]. The growth models of model I are expressed as follows:

$$I_S = I_0^S \exp \left[-(1 - (\alpha_A^S)^m)^\frac{Jt}{m} \right] \quad \cdots \quad (1a),$$

$$I_A = I_0^\infty \left(1 - \exp \left[-(1 - (\alpha_A^A)^m)^\frac{Jt}{m} \right]\right) \quad \cdots \quad (1b),$$
where $I_S$ is the Auger signal from the substrate after passing $Jt$ thick adsorbate layer, and $I_A$ the signal from this adsorbate layer. $J$ is flux density of sticking adatoms and $t$ is deposition time. Also, $I_S^0$ is the Auger signal from the clean substrate, and $I_A^\infty$ the Auger signal from bulk adsorbate. The transmission coefficients $\alpha^A$ and $\alpha^x$ are defined as the transmission probability of Auger electrons originating from the substrate and adsorbate through a single adsorbate layer. By fitting the experimental data with the analytical model I, i.e., Eqs.(1a) - (1b), the variable $m$ can be determined. At $m = 0$ the growth mode corresponds to Frank- van der Merwe growth, at $m = 1$ corresponds to simultaneous multilayer (SM) growth and at $m > 1$ corresponds to Volmer-Weber growth. Also, Stranski-Krastanov (SK) growth mode is described as follows:

$$I_S = I_S^0 \alpha_S^A \exp \left[ -(1 - (\alpha_S^A)^m) \frac{Jt-l}{m} \right], \quad I_A = I_A^\infty \alpha_A^x \left[ 1 - \exp \left[ -(1 - (\alpha_A^x)^m) \frac{Jt-l}{m} \right] \right] \quad \cdots (2),$$

where $Jt > 1$. The inelastic electron mean free path (IMFP) for determination of the transmission coefficients $\alpha$ is calculated by TPP - 2M formula [5], and IMFP values used here are 0.408 nm, 0.517 nm and 1.30 nm, respectively, for Au(69 eV), Se(99 eV) and Te(483 eV) Auger electrons. Also, film thickness corresponding to 1ML was postulated by present LEED results. The 1ML of Se, Se$_{70}$Te$_{30}$, Se$_{50}$Te$_{50}$, Se$_{20}$Te$_{80}$ and Te are 0.126 nm, 0.136 nm, 0.142 nm, 0.151 nm and 0.157 nm, respectively. The transmission coefficients for every 1ML are $\alpha^S_{Se} = 0.671$, $\alpha^S_{Se} = 0.583$, $\alpha^S_{Se} = 0.855$, $\alpha^S_{Se} = 0.551$, $\alpha^T_{Te} = 0.849$, $\alpha^S_{Au} = 0.531$, $\alpha^S_{Se} = 0.841$, $\alpha^S_{Se} = 0.499$, and $\alpha^T_{Te} = 0.836$, $\alpha^T_{Te} = 0.480$.

Theoretical curves shown in Figs. 1a - 1c have been drawn using Eqs. 1a and 1b. By fitting the experimental data with theoretical curves, it can be estimated the initial growth processes of Se$_{100-x}$Te$_x$ alloy films deposited on Au(111) surfaces as follows: Se grows in layer-by-layer growth of $m = 0.1$ for coverage below 1ML, and Se grows in island growth of $m = 1.5$ for coverage until 5ML as shown in Fig. 1a. It is impossible to fit the equation (2) of Stranski-Krastanov mode in experimental data because of the irregular slope of Auger intensity curve in vicinity of 1ML. This irregular slope may be interpreted as a transition or mixing region from layer-by-layer growth to island growth. We have previously pointed out that the growth of Se overlayer on Au(111) follows the layer-by-layer growth until 3rd layer and then the island growth [6]. However, according to the model I, it would be reasonable to modify the previous our conclusion. Also, Se$_{70}$Te$_{30}$ alloy film grows in layer-by-layer growth of $m = 0.1$ for coverage below 1ML, and this alloy film grows in SM growth of $m = 0.6$ for coverage until 5ML as shown in Fig. 1b. Se$_{50}$Te$_{50}$ alloy film grows in SM growth of $m = 1.0$ for coverage until 1ML as shown in Fig. 1c, whereas the fact that the experimental data of Au Auger intensity from 1ML to 4ML deviate from theoretical curve suggests that this alloy film grows in island growth of larger $m$. Se$_{20}$Te$_{80}$ alloy film grows in island growth of $m = 1.9$ for coverage below about 3ML as shown in Fig. 1d, and this alloy film also grows in island growth of larger $m$ from 3ML to 5ML. The reason why the larger $m$ occurs for limited ranges of film thicknesses is not so clear. Te film grows in island growth of $m = 1.9$ for coverage below 4ML, as shown in Fig. 1e, with the exception of irregular points in vicinity of 1ML. Sorenson et al. [7] pointed out that the irregular points in the Au signal in vicinity of 1ML may be associated with roughening transition.

The results stated above suggest that when the composition $x$ increases, the 1ML growth of Se$_{100-x}$Te$_x$ overlayer is shifted from layer-like growth towards island-like growth.

References

1. Kushwaha N, Kushwaha V S, Shukla R K and Kumar A 2005 J. Non-Cryst. Solids 351 3414
2. Nagashima S 2002 J. Crystal Growth 237-239 2055
3. Nagashima S and Otsuka I 1995 J. Crystal Growth 146 266
4. Fu Q and Wagner T 2005 Appl. Surf. Sci. 240 189
5. Tanuma S, Powell C J and Penn D R 1991 Surf. Interface Anal. 17 911
6. Nagashima S 1997 Appl. Surf. Sci. 121-122 116
7. Sorenson T A, Varazo K, Suggs D W and Stickney J L 2001 Surf. Sci. 470 197