成長した GeS 薄膜における複屈折効果の観察
Observation of the birefringent effect on grown GeS thin films

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Abstract

Two-dimensional layered semiconductors, i.e., germanium monosulfide (GeS), have been considered as one of the candidates for developing next-generation functional electronics and optoelectronics [1-3]. Previously, lateral growth of GeS thin films using the pre-deposited amorphous GeS method and fabrication of GeS field-effect transistors (FETs) have been investigated [4-5]. In this study, observation of the birefringent behavior in grown GeS thin films is demonstrated using the cross-polarizer of the optical microscope.

１． Introduction

The discovery of graphene has accelerated the development of a wide range of functional devices using two-dimensional (2D) layered materials [1]. The rediscovery of germanium monosulfide (GeS) as a new group of functional semiconductors including Group IV monochalcogenides, highlights the significant potential for the development of novel applications owing to their unique electronic and optoelectronic properties such as in-plane ferroelectricity, direct bandgap of 1.6 eV, photostrictive properties and so forth [2-3]. Laterally-grown GeS thin films show the significant potential of GeS for use as a key functional material in the development of next-generation electronic and optoelectronic applications such as full-light controlled computing-in-memory devices and sensors. In this study, same as our previous studies [4-5], a novel method that takes Mullins-Sekerka instability into account is utilized to grow GeS thin films using a quartz tube furnace [6]. The crystallization of grown GeS thin films is evaluated by using X-ray diffraction (XRD) measurement and the birefringent behavior is observed by using the crossed-polarizer of optical microscope.

２． Experimental methods

In experiment, a horizontal quartz tube with two independently controlled heating regions is utilized to facilitate the deposition and crystal growth of GeS thin films. The GeS powder is placed in the upstream heating region of the tube, while substrates (e.g., 300-nm-SiO_2/Si and quartz) are positioned in the downstream heating region. The XRD data is collected using a PANalytical X'Per PRO MRD X-ray diffractometer with a Cu Kα source, in the range of 2θ from 10º to 40º with a step of 0.01º. Optical microscope with an angle resolved polarizer is utilized for the observation of the birefringent behavior of grown GeS thin films.

３． Experimental results

The XRD spectra is shown in Fig. 1. It confirms the orthorhombic structure of GeS, in accordance with the standard GeS reference of PDF#00-009-0231. Only the diffraction peaks located at about 16.9º for (002) and 34.2º for (004) are obtained, indicating that the crystal orientation is along with the c-axis, and normal to the van der Waals stacking layers. This suggests that GeS thin films directly grown on SiO_2/Si substrates mainly consist of the layered structure. Optical microscope with an angle-resolved polarizer is utilized for the evaluation of the birefringent behavior of GeS thin films as shown in Figs. 2. The black regions, so-called Maltese extinction crosses as depicted in Fig. 2(b), are the

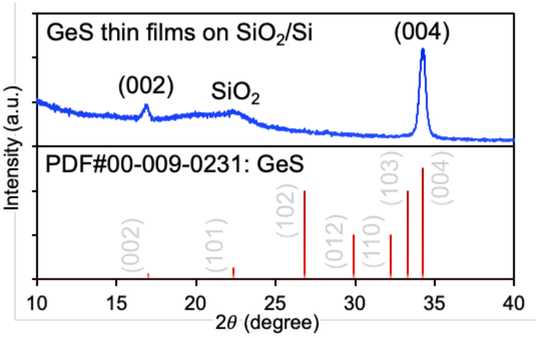

Fig. 1. XRD spectra of GeS thin films

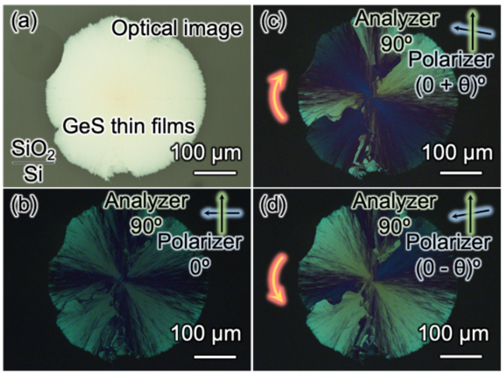

Fig. 2. Observation of the birefringent effect

common characteristic of radial anisotropic body between crossed polarizers. The Maltese-cross is parallel to the polarizer/analyzer orientation of the microscope and independent of the stage orientation. Maltese-cross results from the cancellation of birefringence every 90º with crossed polarizer, hence all the vertical and horizontal crystalline GeS are dark in the observed optical image. With the polarizer slightly rotating by certain angle, one arm of Maltese-cross rotates accordingly as shown in Figs. 2(c-d). The observed features suggest that the grown GeS thin films possess spherulite-like structures, since spherulite-substance exhibits a Maltese-cross pattern observed by optical microscope with a crossed polarizer [7]. It is considered that the green area likely shows the same structural orientation along armchair/zigzag edge as the sub-domain of crystallized GeS, existing in the circular domain of spherulite-like GeS thin films.

The formation of spherulite-like GeS thin films is likely attributed to a sharp local phase gradient exited in the adatom region of growth front among crystallized GeS, GeS vapor source and re-sublimated GeS. The ultrahigh supersaturation induced condensation at the growth front likely results in a lateral growth of spherulite-like GeS at the interface of the sharp local phase gradient. In addition, the growth rate for a nonlinear spherulitic growth is analogous to the supercooling-like method in the order of several micrometers per second [8]. The formed dendrite at the circular periphery likely confirms the Mullins-Sekerka instability which is only limited to the normal growth mechanism for diffusion-limited growth, whereas the spherulite formation at the inner body of GeS is considered to be controlled by kinetic growth since the spherulites do not form under diffusion control. The diffusion-limited growth starts from the growth front at the periphery of the spherulite-like GeS after the nucleation, and then it may exhibit a transformation suddenly into a kinetic-limited growth for the body of spherulite-like GeS thin films. The detailed growth model is under consideration.

4. Conclusions

The birefringent behavior of grown GeS thin films is evaluated in this study. It is suggested that the grown GeS thin films possess spherulite-like structures that holds the potential to achieve single-crystalline GeS, as previously demonstrated with GeO_2 [9], paving the way for the development of next-generation GeS FETs with the potential advantage in programmable of FETs using the optic control method.

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