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Electrical and Optical Properties of GaSe Thin Film Prepared by RF Magnetron Sputtering

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The GaSe thin film has been prepared by RF magnetron sputtering method on fused quartz substrates. The substrate temperature was controlled RT(room temperature) ~600 [℃] during sputtering. The X-ray diffraction peaks of (004) and (008) in hexagonal β-GaSe appeared, when the substrate temperature was over 450 [℃] during sputtering. The structure of crystalline film was oriented perpendicular to the substrate plane. The stoichiometric ratio of the crystalline film was Ga:Se = 1:1. The dark conductivity of crystalline film deposited at 550 [℃] followed the Arrhenius's relation. The activity energy of 0.46 [eV] was estimated.

By the photo conductivity dependence on temperature, the activity energy of 0.2 [eV] was estimated. It may be considered that the value 0.2 [eV] is related with a trapping center level. The optical band gap Eg was estimaited by the measurement of absorption coefficient. The Eg was evaluated as 1.9 [eV] for the amorphous film deposited at RT~300 [℃], and as 2.4 [eV] for the crystalline film deposited at 450 [℃].

1. Introduction

Gallium Selenide(GaSe) thin films have been attracting attention as optical materials for application to dynamic electronic devices.

GaSe is a layered semiconductor of the III-VI compound where each layer contains two Ga and two Se closed packed sublayers in the stacking Ga/Se atoms. The binding of two adjacent layers is of Van der Waals type, while within the bonding is mainly covalent. There have been many reports [1], [2] on the characteristics of GaSe relating to its layered structure, which causes typical optical properties, such as the shift of fundamental band edge. These properties are implied for application to the light modulation. The technics of thin film process are important for application to devices, especially there are a few cases of fabrication and evaluation on GaSe thin films prepared by a plasma process which is favorable for industry. Therefore we have made GaSe thin films by RF magnetron sputtering at 80~600 [℃] of deposition temperature and investigated electrical and optical properties, due to the film structure.

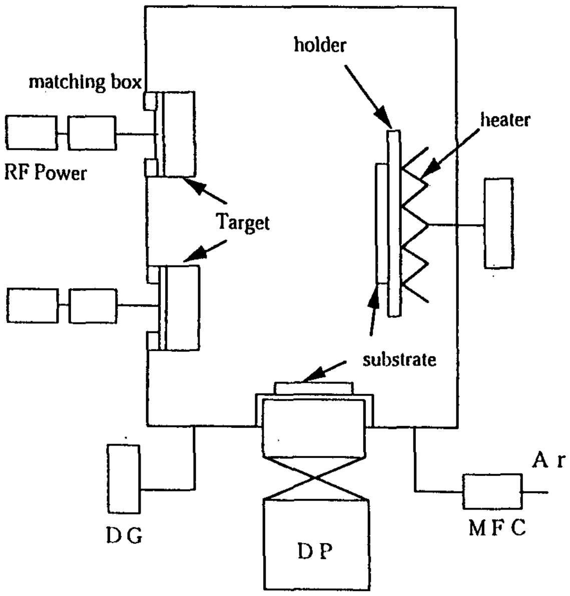

Fig. 1 Schematic Diagram of Sputtering System

2. Experiment

GaSe thin films were prepared by a RF magnetron sputtering method using the SHIBAURA CFS-4ES Sputtering system. The schematic diagram of the experimental equipment is shown Fig. 1. GaSe films were grown on fused quartz. Talystep has been used to measure the thickness of the GaSe films which were deposited on the corning 7059 substrate. The thickness of deposited GaSe films is about 1000 [Å] with the deposition rate 1.8 [Å/sec]. The conditions for deposition of this experiment are shown in Table 1. The vacuum chamber was evacuated by a diffusion and rotary pump system down to 5×10^{-4} [Pa].

Table 1 Growth cnditions of GaSe thin films

Target	: GaSe (99.99 [%])
RF Frequency	: 13.56 [MHz]
RF Power	: 40,100 [W]
Base Pressure	: 5×10^{-4} [Pa]
Ar Gas Pressure	: 0.75 [Pa]
Substrate	: Fused Quartz
Substrate Temperature	: RT~600 [℃]
Film Thickness	: 500~5000 [Å]

Then Ar gas was introduced into the chamber. Ar gas pressure of 0.75 [Pa] was observed by Diaphram Gage. The temperature of substrate was controlled in the range 80~600 [℃] during sputtering. The sputtering target was a high purity GaSe disk of 3 inches in diameter. The power supply unit was 13.56 [MHz] RF generator with a maximum power 500 [W]. The structure of prepared film was measured by the X-ray diffraction method. Optical energy gap was estimated by absorption coefficient α (calculated by the measurement of transmittance) and reflectance in spectra region between infrared and ultraviolet radiation.

The measurement of temperature dependence of dark conductivity was carried out to investigate gap states and conduction mechanisms. Also, band tail states were estimated by measurement of temperature dependence of photo conductivity.

3. Results and Discussion

3-1 Film structure

The crystalline structure of RF-sputtered GaSe films varies from amorphous to crystalline phase, depending on the substrate temperature during deposition. Fig. 2 shows the substrate temperature behavior of X-ray diffraction spectra for the sputtered GaSe film. When substrate temperature was below 300 [℃], the X-ray diffraction peaks were not observed. It was found the amorphous phase to be obtained at the substrate temperature below 300 [℃]. When the substrate temperature reached 450 [℃], the X-ray diffraction peaks of (008) in hexagonal β-GaSe appeared in addition to (004) peak. The structure of crystalline film was oriented prependicular to the substrate plane. SEM measurements were performed to measure the morphorogy (grain size). The SEM image for the GaSe films on fused quartz for several substrate temperatures are shown in Fig. 3, where the grain size are found as large as 100 [nm].

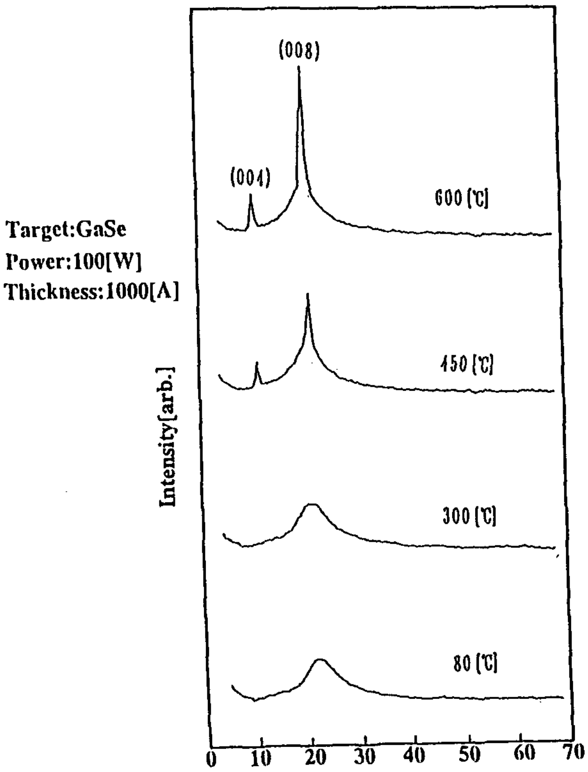

Fig.2 X-ray diffraction patterns of GaSe thin films grown on the fused quartz substrate by RF sputtering at temperature from RT to 600 [℃]

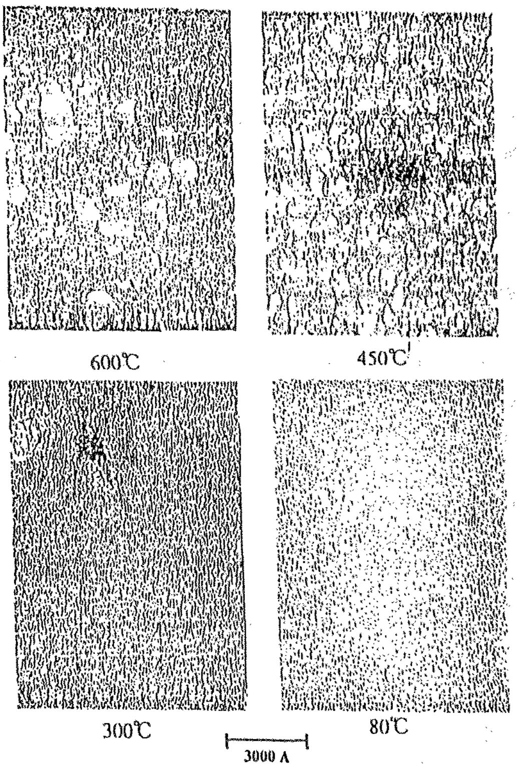

Fig. 3 SEM images of the GaSe thin film on fused quartz with substrate heating at several substrate temperatures (RF power 100 [W]).

3 - 2 *Optical absorption*

We mesurred absorption coefficient of GaSe thin films at room temperature. The optical transmission and reflectivity were measured in the range 1.0~3.5 [eV]. In caluculating the absorption coefficient α, the experimentally determined reflectivity was taken into account. According to the band structure theory of indirect transition, absorption coefficient α is expressed by the following relation

$$(\alpha h\nu)^{1/2} = A(h\nu - Eg) \qquad (1)$$

where, A is a constant and Eg is optical band gap. Eg can be derived from the relation of α and $h\nu$.
The optical gap Eg was determined from the absorption measurement. The energy of the transition is estimated from the plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ (Fig. 4).

We obtained Eg = 1.9~2.4 [eV] for the GaSe films by RF sputtering. Fig. 5 shows the relation of Eg and deposition temperature. Eg increases as the substrate temperature increases.

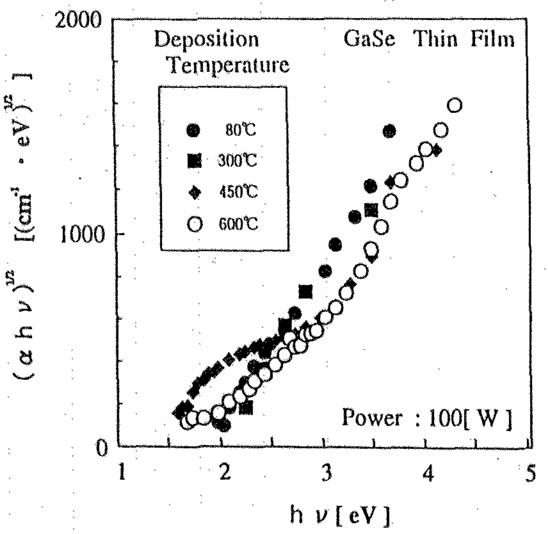

Fig. 4 $(\alpha h\nu)^{1/2}$ as a function of phton energy $h\nu$ between 1.0 and 5.0 [eV] for GaSe films by RF sputtering.

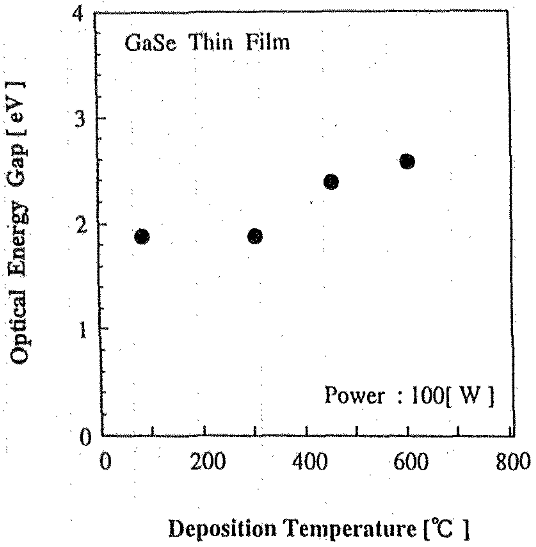

Fig. 5 Dependence of optical energy gap on the deposition temperature of the GaSe films.

The results yield Eg=1.9 and 2.6 [eV] for the substrate temperature at RT and at 600 [℃], respectively. From these results, it is found that the substrate temperature causes some annihilation of the sturctural disorder and reduction in the concentration of localized levels and enlarges the optical gap.

3 - 3 Dark conductivity

Temperature dependences of dark conductivity were shown in Fig. 6. In general, dark conductivity σ_d in the band condition (for semiconductor) depends on temperature according to the equation,

$$\sigma_d = \sigma_0 \exp\left(-\frac{(Ec - Es)}{2kT}\right) \quad (2)$$

where, σ_0 is a constant. Ec is the bottom of conduction or the top of valence band. k is the Boltzmann constant. The temperature range between 140 [℃] and -25 [℃], the data of amorphous films below substrate temperature of 300 [℃] clearly did not lie on a straight line. Because, the conduction mechanism was not of band conduction but it is hopping conduction through localized density of gap states. The characteristics of crystalline films prepared over 450 [℃] indicated the band conduction in all the temperature range (300~-25 [℃]), the activation (Ec-Es) energies of GaSe film prepared at 450 [℃] were 1.3, 1.0 [eV], respectively, and 550 [℃] was 0.9 [eV]. It was deduced that carrier supply level of crystalline films was due to lattice defects or impurity levels.

The Eg was evaluated 1.9 [eV] as the amorphous film deposited at 80~300 [℃], and 2.4 ~2.6 [eV] as the crystalline film deposited at 450~600 [℃]. It was considered to be changing in morphology structure of GaSe thin film prepared by sputtering.

3 - 4 Photo conductivity

Fig. 7 shows the photo conductivity σ_{ph} as a function of reciprocal temperature. The light source used for σ_{ph} measurement was a xenon lamp with 200 [W]. In general, σ_{ph} is expressed by the following relation.

$$\sigma_{ph} = B\exp\left(-\left(\frac{Ec - Et}{kT}\right)\right) \quad (3)$$

In this equation, B is constant. Et is the trapping level below the conduction or above the valence band, corresponding to the tail edge.

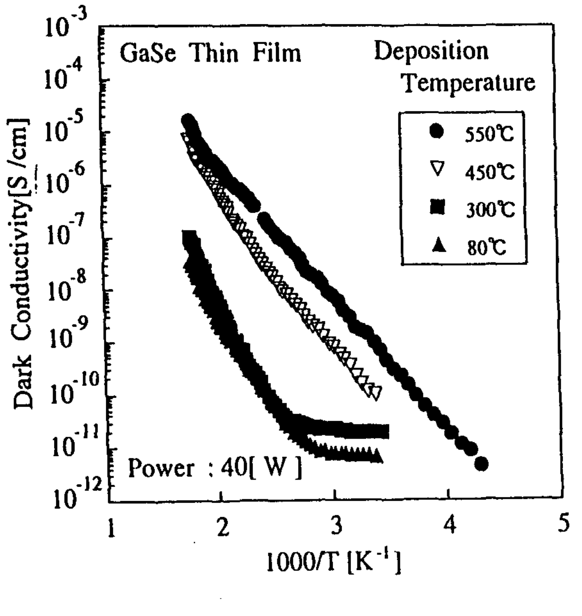

Fig. 6 Arhenius plots of dark conductivity for the RF-sputtered GaSe films.

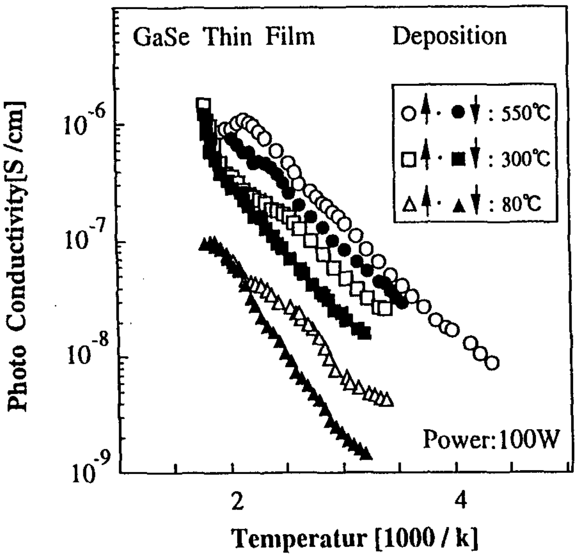

Fig.7 Photoconductivity plotted against the inverse temperature for the GaSe films prepared by sputtering.

The trapping level Et of the film at the deposition temperature of 80 [℃] was 0.35 [eV], at 300 [℃] was 0.23 [eV] and at 550 [℃] was 0.21 [eV].

These show that the width of tail states decreased because of crystallization of the film structure. In this equation, B is constant. Et is the trapping level bellow the conduction or valance band side corresponding to the tail edge.

4. Conclusions

The GaSe thin film has been prepared by RF magnetron sputtering with various substrate temperatures. Electrical and optical properties and film structure were investigated to establish crystalization in the sputtering system. As a consequence, the following results were obtained.

(1) When the substrate temperature reached 450 [℃], the structure of crystalline film was oriented perpendicular to the substrate plane.

(2) The optical band gap Eg was estimated to be 1.9 [eV] for the amorphous films deposited at 80～300 [℃], and 2.4～2.6 [eV] for the crystalline films deposited at 450 ～ 600 [℃].

(3) The conduction mechanism of crystalline film was the band conduction, and the film prepared at 550 [℃] had donor or accepter level of 0.9 [eV] below the bottom of conduction band or above the top of valence band, and the film prepared at 450 [℃] had donor or accepter levels of 1.0 and 1.3 [eV] below the bottom of conduction band or above the top of valence band.

(4) When the deposition temperature increased from 80 [℃] to 550 [℃], the width of band tail decreased from 0.35 [eV] to 0.21 [eV].

Reference

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2) Y. Iwamura, M. Moriyama and N. Watanabe, Jpn. J. Appl. Phys., 30, No. 1A (1991) L42-L44