Study of Amorphous Gallium Arsenide Films Using a Novel Evaporator with Nondestructive Pickup Image and Electron Diffraction Pattern Investigations

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In order to investigate the structure of amorphous gallium arsenide (a-GaAs) targets we developed a novel evaporator attached to an inspection chamber wherein an electron beam serves as both a television (TV) scanning beam and an electron diffraction beam. GaAs targets fabricated by a flash evaporation method at a substrate temperature of above 220°C consist of polycrystalline GaAs (poly-GaAs), the grain size of which is 75 Å, and have an electron mobility of 125 ~ 180 cm²/Vs. GaAs targets fabricated at a substrate temperature below 200°C are amorphous. We identified two bond lengths, 2.48 Å and 4.00 Å, in radial distribution function (RDF) analyses. These values indicate the interatomic bond lengths of Ga-As and Ga-Ga or As-As, respectively. The including angle of an isosceles triangular molecule of As-Ga-As or Ga-As-Ga is 107.5°. The standard deviations of the bond lengths are 0.145 Å for the 2.48 Å peak and 0.348 Å for the 4.00 Å peak. The electron mobility of a-GaAs is 0.17 ~ 0.45 cm²/Vs. The resistivities of poly-GaAs and a-GaAs targets are 10² Ωcm and 10⁷ Ωcm, respectively. Moreover, we achieved a high resolution of pick-up images on an a-Se/a-GaAs target.

1. Introduction

The structure of amorphous materials is often changeable according to the energy of the X-ray diffraction or RHEED if the energy is high. In order to investigate amorphous gallium arsenide (a-GaAs) targets using the electron diffraction of low energy, we developed a novel evaporator attached to an inspection chamber wherein the electron beam itself serves as both a television (TV) scanning beam and an electron diffraction beam. This type apparatus has not been reported until now.

A single-crystalline GaAs is expected to be used in image sensors.¹⁾ However, since a uniform thinning of a GaAs crystal is very difficult because of its fragility, the developments of GaAs targets have been remained stagnant. On the contrary, amorphous materials such as a-Si and a-Se, the lateral resistivities of which are high, are suitable for sensor targets, are in practical use. Amorphous galli-

um arsenide (a-GaAs) was examined in solar cells.²⁾ However, no reports on a-GaAs sensors are available. Neither electrical nor structural properties of a-GaAs have been studied much recently.

Murri reported the electron mobility of a-GaAs formed by the sputtering method to be 8 × 10⁻² cm²/Vs,³⁾ and Park et al. reported the electron mobility of a-GaAs_xP_{1-x} (x < 0.7) to be 0.2 ~ 0.5 cm²/Vs.⁴⁾ The mobilities between the two were inconsistent, although the same method of sputtering used for specimen preparation. Matsumoto and Kumabe studied the relationship between the molecular-beam ratio and the a-GaAs phase.⁵⁾ Their results suggested that a-GaAs was formed with a molecular beam ratio with excess As atoms (1 ~ 3%). Schevchik and Paul reported that the structure of a-GaAs is similar to that of amorphous germanium.⁶⁾ As mentioned above, the mobility determined by Murri is rather small for an imager diode and the specimen composition determined by

Fig. 1 Structure of the evaporator with an inspection chamber.

Park et al. is not pure GaAs. Thus the mobility of a-GaAs must be studied in detail. A reproducible method fabricating a-GaAs with larger mobilities than the above values must be established.

The present authors devised an advanced reproducible method using flash evaporation within a hot-wall cylinder, and obtained mobilities larger than Murri's value. We clarified the relationships between the substrate temperature and the amorphous phase. We also report here on the mechanism of the novel apparatus and on electrical, structural, and imaging properties of a-GaAs targets determined using it.

2. Experimental

2.1 Structure of apparatus

Figure 1 shows the structure of the novel apparatus. The bell jar (a) of the evaporator is evacuated to below 10^{-5} Pa by a diffusion pump (e) and a rotary pump (f). The specimen (k) is fabricated on a substrate (b) of glass or CaF_2 in the hot-wall cylinder (d). The specimen is mounted in a specimen holder (c). On top of the specimen holder is a ring of stainless steel (SUS-410) via which the specimen and specimen holder can be easily lifted to the sliding stage (i) in the inspection chamber (g), using an electromagnet. The inspection chamber is attached to the bell jar of the evaporator, which is constantly evacuated by a turbomolecular pump (n) to below 10^{-5} Pa. (m) in Fig. 1 indicates a pickup tube, the deflecting coil (l) of which is electromag-

netic. The elimination of stray capacitance is important in the video amplifier. The overall stray capacitance can be made less than 1 pF, which is shown in the appendix.

(o) in Fig. 1 indicates the specimen inspection unit for electron diffraction measurement, which includes the specimen and a phosphorescent screen (j). Cadmium sulfide is applied on the indium tin oxide (ITO)-coated glass substrate. In the diffraction mode, the specimen is evaporated on a metal mesh substrate, and the incident electron beam is diffracted by the specimen. In the diffraction mode, the surface potential of the screen is higher than the primarily crossover of the secondary emission ratio ($\delta:\delta>1$). The potentials of the screen, the specimen and the mesh range from 1000~2000 V. On the contrary, in the normal TV mode, the potential of the target surface becomes cathode potential because the secondary emission ratio is less than unity. The specimen potential across the two sides of the target is 5~8 V in the TV mode. The intensity profile of the diffracted electron beam was measured using a Faraday cage and photographic measurement. Moreover, in the case of the highly sensitive measurement, a novel electron-beam-induced conduction image intensifier was used.⁷⁾

2.2 Sample preparation

We fabricated GaAs targets by a flash evaporation method within a hot-wall cylinder. A substrate of ITO-coated glass or calcium fluoride (CaF_2) cut in a random orientation was mounted in the specimen holder. The temperature of the hot wall was higher than that of the substrate. The degree of exfoliation of GaAs targets on CaF_2 substrates was less than on glass substrates. The boat for evaporating source material was a basket of wolfram wire coated with alumina. A measured amount of GaAs powder was rapidly evaporated in the hot-wall cylinder at a deposition rate of $1 \mu\text{m}/\text{min}$.

Figure 2 shows the arrangement of specimens for mobility measurement with the Hall effect. Each specimen was fabricated by a mask method. The specimens for electron diffraction measurement were evaporated on to the metal mesh substrate. Although resistivities of a-GaAs are decided by the Hall effect, we also examined another evaluation method for resistivities of a-GaAs using electron scanning beam measurement, a theoretical discussion of which is represented in a later section. In this specimen, the amorphous selenium (a-Se) layer ($1 \mu\text{m}$) and a-GaAs layer ($100\sim700 \text{ \AA}$) were successively evaporated on to the ITO-coated glass.

Fig. 2 Arrangement of specimen for mobility measurement with Hall effect.

2.3 RDF analyses

The radial distribution function (RDF) for amorphous materials is expressed as

$$\text{RDF} = 4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + 2r/\pi \int s \cdot \text{Im}(s) \times \exp(-Bs^2) \sin(sr) ds, \quad (1)$$

where r is the length from the center of a given atom to the surrounding atom, $\rho(r)$ is the numbers of atom per unit volume at r , ρ_0 is the average atomic number, Im is the amorphous molecular term for a coherently diffracted electron beam, s is $4\pi \sin \theta / \lambda$, θ is the Bragg angle, λ is the wavelength of the electron beam and B is the artificial temperature factor.⁸⁾ In the RDF analysis, $\text{Im}(s)$ is determined from experimentally obtained halo patterns by subtraction of the components of nonelastic scattering, substrate scattering, and atomic scattering factors. In this subtraction we obtained a corrected $\text{Im}(s)$ using a Fourier transformation filter.⁹⁾ The result of subtraction is evaluated in terms of the degree of linearity of the RDF, where $r < 2.49 \text{ \AA}$, as shown in a later section. The peak shape of the RDF is expressed as

$$4\pi r^2 \rho(r) = N_i \exp(-(r - r_i)^2 / \text{sqr}(4\pi(A_i + B))), \quad (2)$$

where N_i is the number of i -th bonds, $2A_i$ is the standard deviation of the fluctuation of the r_i bond length and B is an artificial temperature factor.

3. Experimental results

The electron mobility of GaAs is shown in Fig.

Fig. 3 Mobility of GaAs targets.

3. The electron mobility of GaAs film fabricated at a substrate temperature of less than 210°C is $0.17 \sim 0.45 \text{ cm}^2/\text{Vs}$, and the resistivity of GaAs is $10^7 \Omega\text{cm}$. The electron mobility at substrate temperatures higher than 210°C is $125 \sim 175 \text{ cm}^2/\text{Vs}$, with a resistivity of $10^2 \Omega\text{cm}$. These differences are related to the structural difference. GaAs targets at substrate temperatures below 210°C are amorphous, whereas those fabricated at substrate temperatures above 210°C are crystalline, as determined from electron diffraction patterns. The electron mobility of a-GaAs determined in our experiments exceeds the $8 \times 10^{-2} \text{ cm}^2/\text{Vs}$ determined by Murri,³⁾ but is close to those obtained by Park et al.⁴⁾

In low-velocity scanning, the surface potential of the target reaches a state of equilibrium of the cathode potential (almost nearly zero). Then the voltage of the target becomes the actual target voltage. Figure 4 shows the relationship between the applied voltage and the photocurrent for a-Se/a-GaAs targets with the structure which was described in 2.2. The photocurrent for R light (wavelength, $\lambda = 6000 \text{ \AA}$) increases with the applied voltage, whereas that for B light ($\lambda = 4500 \text{ \AA}$) shows saturation characteristics. The lack of saturation for R light is due to geminate recombination.¹⁰⁾ If the target is fabricated with only a single layer of a-Se without a-GaAs, then the whole landing electron beam flows into the a-Se layer, and the enormous dark current independent of incident light becomes more than 200 nA , since the rectifying action vanishes. In this case, no photocurrent could be observed. However, in Fig. 4, at first sight, the dark current seems to be a little large. We used a high-power electron gun, the optical stray radiation of which was much stronger than the normal low-power gun. We confirmed that the dark current was suppressed to below 10 nA if the optical radiation of the cathode is decreased by tem-

Fig. 4 Relationship between applied voltage and photocurrent for a-Se/a-GaAs.

porarily decreasing filament currents as shown in dashed line in Fig. 4. In addition, the recovery speed of the target with an a-GaAs layer was much faster than a normal electron-beam-blocking layer of Sb_2S_3 ,¹¹⁾ even if the negative image was produced due to the deficiency of the scanning electron beam, which was induced on a temporary strong light. Thus, the a-GaAs layer is a good electron-beam-blocking layer. The limiting resolution varies with the thickness of the a-GaAs layer (namely, interpixel resistance). If the thickness of the a-GaAs layer is less than 700 Å, the limiting resolution is more than 500 TV lines; the theoretical discussion of the relationship between film thickness and limiting resolution is shown in a later section.

The molecular term for electron diffraction obtained using this apparatus is shown as a function of s . Figure 5 shows the relationship between r and RDF. There is no ripple in the range of $0 \text{ Å} < r < 2.49 \text{ Å}$ in Fig. 5, which shows that the correction of $\text{Im}(s)$ shown in 2.3 is valid. Since the range of s of the measured diffraction is twice that of s of a $\text{CuK}\alpha$ line, the image of RDF obtained using this apparatus is remarkably clear. Moreover, no structural changes are detected using electron beams.

4. Discussion

4.1 Molecular structure of a-GaAs

We identified two distinct peaks in Fig. 5 by using eq. (2). The first bond length (2.48 Å) is 1.64% larger than the bond length (2.44 Å) determined from the atomic radii of Ga (1.26 Å) and As (1.18 Å).¹²⁾ The value of the first peak is the same as that determined by Shevchick and Paul;⁹⁾

Fig. 5 Relationship between r and RDF.

however, the second bond length (4.0 Å) is smaller than the one they determined (4.10 Å). These two peaks (2.48 Å, 4.0 Å) indicate the bond lengths for a tetrahedral molecule of a-GaAs. The including angle of an isosceles triangle molecule of As-Ga-As or Ga-As-Ga is $\cos^{-1}((b^2 - 2a^2)/2a^2)$ (107.501°), where $a=2.48$ and $b=4.0$.

If the tetrahedral molecule is made of monatomic or effectively monatomic atom as shown in Fig. 6, then the following equations stand.

$$2r \cos(\alpha) = a/2, \quad (3)$$

$$a/2 = h \cos(30^\circ), \quad (4)$$

$$(2ro)^2 = h^2 + x^2, \quad (5)$$

$$a^2 = (2ro + x)^2 + h^2, \quad (6)$$

where ro is the atomic radius, x is the height of the center atom in a tetrahedron and h is the length from one corner to the center of a triangular face. By replacing h and x by a and r , α and θ are obtained as 35.264° , and 109.471° , respectively.

The angle 107.501° shows that the actual tetrahedron deforms -1.8% from a monatomic amorphous one (109.471°). The discussion above can be applicable to amorphous binary alloys. If the probability for a Ga atom or As atom occupying an atomic position of a tetrahedron is exactly fifty percent, then the angle may become 109.471° as does that of GaAs crystal. The angle 107.501° may show the existence of the excess As atom from stoichiometry. The chemical analysis showed that the ratio of Ga and As in a-GaAs was 1.0 and 1.08, respectively. Our result may coincide with the suggestion of Matsumoto and Kumabe.⁵⁾ In future we will investigate the precise composition in other method.

4.2 Design of the resistive sheet of a-GaAs

Let both pixel size and interpixel size be L , and the thicknesses of a-Se and a-GaAs be d_1 and d_2 ,

Fig. 6 The model of a tetrahedral molecule.

respectively. Then the interpixel potential difference (δV) changes after a unit accumulation time:

$$\delta V = V_{\text{initial}} \exp(-t/\tau), \quad (7)$$

where V_{initial} is the interpixel potential difference determined by the optical pattern. The time constant (τ) of the discharge of accumulated charges in two adjacent pixels is

$$\tau = \epsilon_0 \epsilon_r L^2 \rho / (d_1 d_2), \quad (8)$$

where ϵ_0 is a dielectric constant of vacuum, ϵ_r is the relative dielectric constant of a-Se (5.0) and ρ is the resistivity of a-GaAs ($10^7 \Omega\text{cm}$). Figure 7 shows the relationship between the thickness of a-GaAs and pixel size. The L corresponding to 500 TV lines is $20 \mu\text{m}$. If $\tau \geq 1/30 \text{ s}$ at $L = 20 \mu\text{m}$, then the optimal thickness for high resolution (more than 500 TV lines) is less than $700 \text{ \AA}$. The black circles in Fig. 7 represent the thicknesses of a-GaAs sheets which result in the experimentally high resolution obtained by changing the rate of charge accumulation. The coincidence between the calculated and experimental results is good, and confirms the accuracy of the values of ρ determined in Hall measurements.

5. Conclusion

In order to investigate the structure of a-GaAs targets we developed a novel evaporator attached to an inspection chamber, wherein an electron beam serves as both a television (TV) scanning beam and an electron diffraction beam.

(1) GaAs targets fabricated by a flash evaporation method at a substrate temperature above 220°C consist of a polycrystalline GaAs, the grain size of which is $75 \text{ \AA}$, and have an electron mobility of $125 \sim 180 \text{ cm}^2/\text{Vs}$.

(2) GaAs targets fabricated at a substrate temperature below 200°C are amorphous. We identified two explicit bond peaks, $2.48 \text{ \AA}$ and $4.00 \text{ \AA}$,

Fig. 7 Relationship between thickness of a-GaAs and pixel size. Appendix:

by RDF analyses. These values indicate the interatomic bond lengths of Ga-As and Ga-Ga or As-As, respectively.

(3) The including angle of an isosceles-triangular molecule of As-Ga-As or Ga-As-Ga is 107.5° , whereas that for a monatomic amorphous one is 109.472° . The standard deviations of bond lengths are $0.145 \text{ \AA}$ for the $2.48 \text{ \AA}$ peak and $0.348 \text{ \AA}$ for the $4.00 \text{ \AA}$ peak.

(4) The electron mobility of a-GaAs is $0.17 \sim 0.45 \text{ cm}^2/\text{Vs}$.

(5) The resistivities of GaAs and a-GaAs are $10^2 \Omega\text{cm}$ and $10^7 \Omega\text{cm}$, respectively.

(6) Good pickup imaging characteristics of an a-GaAs sheet on an a-Se target, the dark current of which is less than 10 nA at a saturation target voltage (3 V), were obtained.

Our apparatus is useful for studies of target materials. In future, we will report on the properties of GaAs and improved sensor devices of GaAs targets in greater detail.

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Appendix:

1. Method of decreasing stray capacitance:

Fig. 8 Relationship between I_s and SN ratio for various stray capacitances.

In the design of the TV amplifier for the inspection chamber, the stray capacitance of the wiring, around the specimen and specimen holder, to the earth must be eliminated since the signal-to-noise (SN) ratio becomes small if it is large. When a metallic stage was used, the overall stray capacitance between the stage and the specimen holder reached more than 300 pF. In an attempt to eliminate the stray capacitance, we used an insulating stage. As for vacuum insulator materials, glass is fragile, and Teflon or Derlin lack sufficient hardness. Acrylic resin has high hardness, but exhibits out-gassing in vacuum. However, there is a report of applying acrylic resin to an electric insulating tool in vacuum.¹³⁾

First we made the sliding stage out of acrylic resin in order to decrease the stray capacitance. The amount of out-gassing of acrylic resin is small, and it can be used for the sliding stage at below 10^{-5} Pa after it is baked at 60°C for 10 min. The stray capacitance between the stage and the specimen holder is decreased to 20 pF, since the stage is an insulator. However, the wiring from the specimen to the preamplifier that located outside of the chamber, remains an issue. We mounted the entire preamplifier in the vacuum. We selected specific electric parts, such as the field effect transistor (FET), resistor and titanium condenser, which are durable in vacuum usage. Problems related to out-gassing and thermal heating do not arise in this method, and the overall stray capacitance becomes less than 1 pF.

Fig. 9 Relationship between screen size (x) and s .

2. Effect of the stray capacitance on SN ratio

The theoretical characteristics of the SN ratio, taking account of stray capacitance, are

$$\text{SN ratio} = I_s / \sqrt{2eI_sB + I_{\text{amp}}}, \quad (1)$$

$$I_{\text{amp}} = 4kTB/R + 4kTBRe(1 + 4\pi^2R^2C^2B^2/3)/R^2, \quad (2)$$

where e is the electric charge, I_s is signal current, B is bandwidth, R_e is the equivalent-noise resistance, R is the input resistance of the FET and C is the stray capacitance.¹⁴⁾ Figure 8 shows the relationship between I_s and the SN ratio, where R_e is 100 Ω and R is $2 \times 10^6 \Omega$. In the case where the preamplifier is located outside the vacuum, the SN ratio is smaller than that in the case of full shot noise at $I_s = 300$ nA, since the stray capacitance becomes 20~50 pF. The ideal SN ratio is shown for the case of full shot noise, where the total noise contained by the signal currents consists of only photon noise. The SN ratio in the case where the preamplifier is in vacuum is close to that in the case of ideal full shot noise, since the stray capacitance is less than 1 pF.

3. Design of the specimen inspection unit for electron diffraction measurement

The specimen inspection unit consists of a screen and the specimen for the sake of compactness. It is important for the design of an electron diffraction apparatus for amorphous materials to increase the maximum value (S_{max}) of $s = 4\pi\sin\theta/\lambda$,⁸⁾ where θ is the Bragg angle and λ is the wavelength of an electron beam. Let the length from the specimen to the screen be named the camera length (H), and let the screen size be x . Then

$$\theta = \arctan(x/H)/2, \quad (3)$$

$$s = 4\pi \sin \theta / \lambda. \quad (4)$$

Substituting eq. (3) into eq. (4),

$$s = 4\pi \sin (\arctan (x/H)/2) / \lambda. \quad (5)$$

If the accelerating voltage, electron mass and Planck's constant are E , m and h , respectively, then

$$\lambda = h / \sqrt{2mE}. \quad (6)$$

Equation (5) is expressed as the polynomial expansion of the term of x/H . **Figure 9** shows the relationship between the screen size x and s , where $H=30$ mm and the error at $x=25$ mm is less than 0.9 %. $S_{\max}$'s for $x=25$ mm at 2000 V and 1000 V are 15.6 and 11.0, respectively. Since $S_{\max}$ in the Cu-K_α X-rays (1.5405 Å) is $4\pi \sin (\pi/2) / 1.5405$ ($=8.157$), $S_{\max}$ at 2000 V is twice that with Cu-K_α X-rays.

When the incident beam current is 300 nA, and the voltage applied to the specimen is 2000 V, the beam power is $6 \cdot 10^{-4}$ W, whereas the incident beam current and the voltage are 10^{-5} A and 10^5 V, respectively; the beam power of RHEED is 1 W. The radiation damage in our apparatus may become less than that of RHEED. In fact, no structural change due to electron beam radiation can be detected.

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