Electrical and optical properties of annealed gallium arsenide thin films on glass substrates

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The effects of annealing in vacuum on the electrical and optical properties of GaAs thin films deposited by the flash evaporation method were studied. Thin films of compound GaAs deposited upon glass substrates at room temperature were annealed in a vacuum of 2×10^{-6} torr at different temperatures up to 350° C. The properties of the films depended strongly on annealing temperature. The lowest resistivity measured was about $1.6 \times 10^4 \Omega$ cm at an annealing temperature of about 240° C. The activation energy of as-deposited and annealed films were measured and compared. Optical absorption measurements of the as-deposited samples and the samples annealed at a temperature of 240° C were made as a function of photon energy.

1. Introduction

Recently keen interest has been shown in the preparation and examination of thin films of semiconducting materials. Gallium arsenide (GaAs) may be considered as a potential competitor of silicon, because of its striking physical properties. The conventional vacuum evaporation method is difficult to apply to compound semiconductors, which dissociate on heating, particularly GaAs and the resulting films are not free from stoichiometric defects. The technique of flash evaporation was developed by Harris and Siegel [1]. This method is generally used for the evaporation and deposition of the compound GaAs. Since the material is evaporated quickly, the decomposition of the compound is minimized. An up to date survey of the literature shows that a few studies of GaAs films on single crystal surfaces of Ge, GaAs and CaF₂ obtained by flash evaporation have been reported [2-4]. Only Pankey and Davey [5] have studied the structural and optical properties of thin GaAs films on glass substrates deposited by this technique. There is, however, little information available on the electrical and optical properties of annealed films of GaAs deposited onto glass substrates by flash evaporation. The purpose of this paper is to present experimental results on electrical and optical properties of asdeposited and annealed films of GaAs obtained by using the technique of flash evaporation.

2. Experimental details

Thin films of compound GaAs were prepared using an Edwards High Vacuum (Crawley, UK) coating unit model E306 with an arrangement for flash evaporation. The compound GaAs of high purity grade was obtained from Ultra-pure Chemical Corporation (New York, USA). The substrates were glass, which were cleaned with chromic acid, alcohol and in ultrasonic cleaner. Prior to film deposition, the substrates were degassed in high vacuum at a temperature of 250° C for 30 min and cooled down slowly to the room

temperature before evaporation. The substrate was placed at a distance of 10 cm from the evaporator. Flash evaporations were carried out when powdered GaAs was allowed to fall slowly onto the previously heated tantalum cup of about 1400° C. The rate of powder flow was adjusted by using a vibrator. The pressure during evaporations was maintained at about 5×10^{-6} torr. The mean film deposition rate was about $2 \,\mathrm{nm}\,\mathrm{sec}^{-1}$. The evaporator temperature was determined by an optical pyrometer. The annealing of GaAs films was carried out at a pressure of about 2×10^{-6} torr in the same vacuum coating unit. The temperature covered in the experiments was from room temperature to 350° C. The effective period of annealing was 1 h in all the experiments. The heating and cooling rates were $2^{\circ} C \min^{-1}$.

Electrical resistivity measurements were performed on GaAs samples by the van der Pauw method [6]. Ohmic contacts were made using indium evaporated under high vacuum. A Keithly 610 C solid state electrometer and Hewlett Packard model 412 A DC multimeter with high input impedance were used for resistivity measurements. A chromel-alumel thermocouple was used to measure the substrate temperature. The conductivity σ and thermoelectric power of GaAs samples with respect to gold was measured as a function of temperature within the range between 303 and 400 K. The thicknesses of the films were measured using Tolansky's interferometric method [7].

Optical absorption measurements of GaAs samples were made in the wavelength range 0.50 to 0.90 μ m of photon energy, using a Shimadzu UV-180 doublebeam spectrophotometer. After taking absorption measurements of as-deposited samples, the films were then annealed at a temperature of 240° C in a vacuum of approximately 2 × 10⁻⁶ torr for 1 h. The absorption measurements were then repeated. The absorption spectra thus obtained were not corrected for reflection losses. High absorption levels being used, the reflection correction is not so important. From the



absorption data the absorption coefficient, α , was calculated and the optical energy gaps were determined graphically.

3. Results and discussion

The room temperature resistivities of the GaAs films were found to vary between 6×10^7 to $1.3 \times$ $10^7 \Omega$ cm for thicknesses between 0.10 to 0.40 μ m. These results are close to those of Segui et al. [8] of GaAs films obtained by plasma deposition method. The films deposited at room temperature were slightly transparent and dark grey and they appear to be stable under ordinary atmospheric conditions. Fig. 1 shows the changes in resistivity as a function of annealing temperature for the samples of $0.25 \,\mu m$ thick. The dependence of the resistivity on the annealing temperature may be interpreted in terms of structural properties of the films. From Fig. 1 it is observed that the resistivity of the films do not increase with increasing annealing temperature up to about 200° C and then after 200° C decrease rapidly. This sudden variation is thought to be due to the changes in crystallinity of the films. The lowest resistivity measured was about $1.6 \times 10^4 \,\Omega cm$ for the annealing temperature of about 240° C. With a further increase of the annealing temperature the resistivity increased remarkably. This sharp increase in resistivity may be due to the increase in grain size because the samples became more transparent when the annealing temperature is higher than 250° C. Similar variations in resistivity with annealing temperature in vacuum have been observed by Kumabe and Matsumoto [9] for GaAs films obtained by an r.f.-sputtering method. However, the crystallization temperature they reported

Figure 1 The changes in resistivity of GaAs films as a function of annealing temperature in vacuum.

is 400 to 450° C and is rather higher than that of the present work. Because of high resistivity, it was not possible to measure the Hall effect of the GaAs films annealed at temperature 240° C. The conduction of the as-deposited samples and the samples annealed at a temperature of 240° C is found to be p-type, as indicated by the thermoelectric power measurements. These results are not in agreement with Yamashita et al. [10] who found that the films thinner than $1 \,\mu m$ exhibited n-type conductivity which was obtained by the simultaneous evaporation method but in agreement with Davey and Pankey [11] who obtained GaAs films by the three temperature zone method. The variation of conductivity σ with temperature for asdeposited samples and the samples annealed at a temperature of 240° C is shown in Fig. 2. From Fig. 2 it is seen that the plots of $\log_{10}\sigma$ against $10^3/T$ obtained are straight lines between room temperature and 400 K. The values of activation energy for the samples deposited at room temperature was 0.45 eV but that of the annealed samples at 240° C was 0.62 eV. The activation energies of as-deposited samples and the annealed samples are found to be about half of the optical energy gaps (Fig. 3). Thus it appears that the Fermi levels of the as-deposited samples and annealed samples are located near the middle of the optical energy gaps. The activation energy of as-deposited samples in our investigation agrees well with those of amorphous GaAs films obtained by molecular beam deposition [12]. The activation energy 0.62 eV of annealed samples are close to that of bulk value of GaAs [13].

The behaviour of the absorption coefficient α of GaAs samples deposited at room temperature and



Figure 2 The plots of $\log_{10} \sigma$ against $10^3/T$ of GaAs films deposited at room temperature and the annealed films which were obtained after annealing the as-deposited films for 1 h at 240° C in vacuum. (•) before annealing, (O) after annealing.



Figure 3 The variation of the optical absorption as a function of photon energy for GaAs films deposited at room temperature and the annealed films which were obtained after annealing the asdeposited films for 1 h at 240° C in vacuum. (•) before annealing, (\odot) after annealing.

the as-deposited samples annealed at a temperature of 240° C as a function of photon energy (hv) are shown in Fig. 3. The optical energy gap of asdeposited samples, for the indirect allowed transition has been determined graphically by plotting $(\alpha h v)^{1/2}$ against (hv) and extrapolating the linear portion to $\alpha = 0$. But the variation of α of annealed samples are indicative of direct transition and it appears that the variation of $(\alpha hv)^2$ against (hv) offers the best fit to the optical absorption data. The values of optical band gap of the as-deposited and the annealed samples are 0.92 and 1.33 eV, respectively. Our results of optical gap for the as-deposited samples and the annealed samples are comparable with the value of amorphous GaAs films [12] and the bulk value of about 1.37 eV [14], respectively. Thus we are in agreement with the report published by Yamashita et al. [10] that the optical gap considerably approached the bulk value when the samples were crystallized.

4. Conclusions

The experimental results show that the films deposited on glass substrates at room temperature are amorphous and the as-deposited films annealed at a temperature of 240° C in a vacuum of 2×10^{-6} torr are polycrystalline. All the as-deposited films and the films annealed at a temperature of 240° C are characteristic of p-type conduction.

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