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Preparation of pulse plated GaAs films

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Abstract

Thin GaAs films were prepared by pulse plating from an aqueous solution containing 0.20 M $GaCl_3$ and 0.15 M As_2O_3 at a pH of 2 and at room temperature. The current density was kept as 50 mA cm^{-2} the duty cycle was varied in the range 10–50%. The films were deposited on titanium, nickel and tin oxide coated glass substrates. Films exhibited polycrystalline nature with peaks corresponding to single phase GaAs. Optical absorption measurements indicated a direct band gap of 1.40 eV. Photoelectrochemical cells were made using the films as photoelectrodes and graphite as counter electrode in 1 M polysulphide electrolyte. At 60 mW cm^{-2} illumination, an open circuit voltage of 0.5 V and a short circuit current density of 5.0 mA cm^{-2} were observed for the films deposited at a duty cycle of 50%.

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Keywords: A. Thin films

1. Introduction

Solar cells used in space have to be highly efficient, lightweight and highly radiation tolerant. To achieve high efficiency, cascade tandem structures with III–V materials such as $In_{0.5}Ga_{0.5}P$ and GaAs epitaxial layers grown on GaAs or Ge substrates have been adopted [1,2]. The solar cells using these III–V semiconductor materials also have better radiation tolerance compared with those made of Si. However, to improve the tolerance further, it is necessary for the cells to attach a cover glass on the surface of a bare cell. This integration results in an increase of the total weight of a solar cell panel.

Since space developments are now reaching a practical and commercial stage rather than the previous scientific or military one, reducing the cost of space missions is one of the most important issues. Therefore, space solar cells should be low-cost in addition to the requirements mentioned above. However, substrates of single-crystal semiconductor materials such as GaAs and Si are quite expensive. In addition, the substrates, which are thick, are generally of no use for a photovoltaic effect since III–V semiconductors have relatively high absorption coefficient in the wavelength range of solar radiation. A thickness of a few microns is sufficient for a solar cell. Several techniques like flash evaporation [3], VPE [4], MBE [5], chemical beam epitaxy [6], spray pyrolysis [7], sputtering [8–12], pulse laser ablation [13], have been used for the deposition of GaAs films. In this work, the periodic pulse technique has been successfully employed for the deposition of GaAs thin films. Though there is a preliminary paper on pulse electrodeposited GaAs films [14], a systematic study of the effect of duty cycle has been done for the first time. This paper reports the results on the properties of pulse electrodeposited GaAs films.

2. Experimental methods

Thin GaAs films were prepared by plating an aqueous solution containing 0.20 M $GaCl_3$ and O.15 M As_2O_3 at a pH of 2 and at room temperature. The current density was kept as 50 mA cm^{-2}, the duty cycle was varied in the range 10–50%. The system used for generating current pulses was a microprocessor controlled pulse plating system. The ON time was varied in the range of 3 s–15 s and the corresponding OFF time was varied in the range

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27 s–15 s. This resulted in duty cycles in the range 10–50%.The films were deposited on titanium and tin oxide coated glass substrates. The plating time was 20 min.Thickness of the films estimated by gravimetry varied in the range of 1.0–2.0 μm as the duty cycle increased from 10–50%. For the set of conditions employed in this investigation the maximum thickness of 2.0 μm was obtained. Films deposited on conducting glass substrates were used for optical band gap determination from absorption measurements. Films deposited on titanium substrates were used for photoelectrochemical measurements.

The films deposited on titanium and tinoxide substrates were characterized by X-ray diffraction technique. Films exhibited polycrystalline nature with peaks corresponding to single phase GaAs. The intensity of the peaks were found to increase with increase of deposition current density. SEM studies indicated that the grain size decreased with current density. Laser Raman studies were carried out on the films using Renishaw LABRAM laser Raman spectrometer. XPS studies were made using VG ESCALAB MKII spectrometer with MgKα radiation.

3. Results and discussion

Fig. 1 shows the X-ray diffraction results obtained from films which were deposited on titanium substrates at different duty cycles, since the XRD patterns of the films deposited on conducting glass substrates were identical to the data obtained on films deposited on titanium substrates only data for the films deposited on titanium substrates are presented in Fig. 1. Diffraction peaks are clearly observed and are located in positions consistent with those expected for GaAs, as indicated by the Joint Committee on Powder Diffraction Standards (JCPDS). Debye–Scherrer equation indicates that the diffraction comes from GaAs crystallites of roughly 70 Å in size for higher duty cycles ranging from 25–50%. The film grown with duty cycles of 10 and 15% also shows weak diffraction coming from ~15 Å crystallites. The low diffraction quality is in part due to the size of the crystallites and to the low material yield at these low duty cycles. This type of behaviour was observed work on pulse plated CdSe films [15].

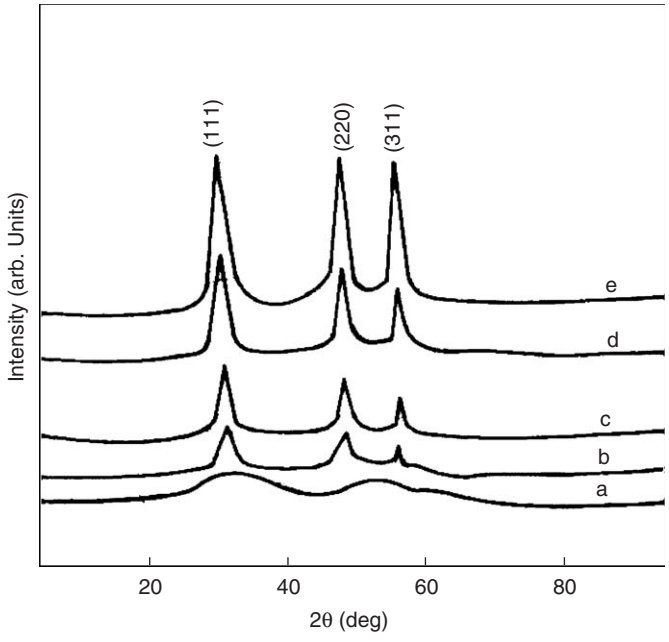

Fig. 1. X-ray diffraction pattern of GaAs films deposited on titanium substrates at different duty cycles (a) 10%, (b) 15%, (c) 25%, (d) 35%, (e) 50%.

According to Moss [16], the optical bandgap of direct-gap semiconductor material can be deduced from the linear relation between the square of absorption coefficient and the photon energy. The absorption coefficient of the films deposited on conducting glass substrates was derived from the optical reflectance and transmittance measurements. The plot of photon energy, hν (h: Plank constant, ν frequency), versus the square of absorption coefficient, α^2, as shown in Fig. 2, indicated that the bandgap (x-intercept) of the film is about 1.4 eV for the films deposited at a duty cycle of 50%. This value suggests that the film can be used as an equivalent solar cell material to single-crystal GaAs. The variation of band gap with duty cycle is indicated in Table 1. It is observed that as the duty cycle increases from 10–50%, the band gap value decreases from 2.02 to 1.40 eV. This is due to the decrease in particle size with decrease of duty cycle. The variation of band gap at

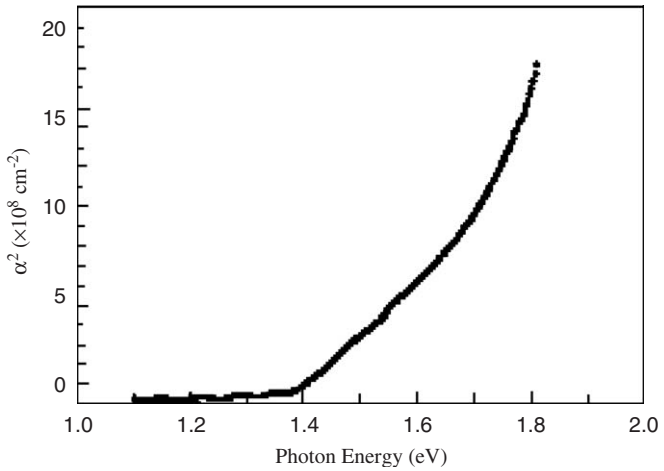

Fig. 2. $(\alpha h\nu)^2$ vs $h\nu$ plot for the GaAs films deposited on conducting glass at a duty cycle of 50%.

Table 1
Variation of band gap with duty cycle

Duty cycle (%)	Band gap (eV)
10	2.02
20	1.88
30	1.72
40	1.63
50	1.40

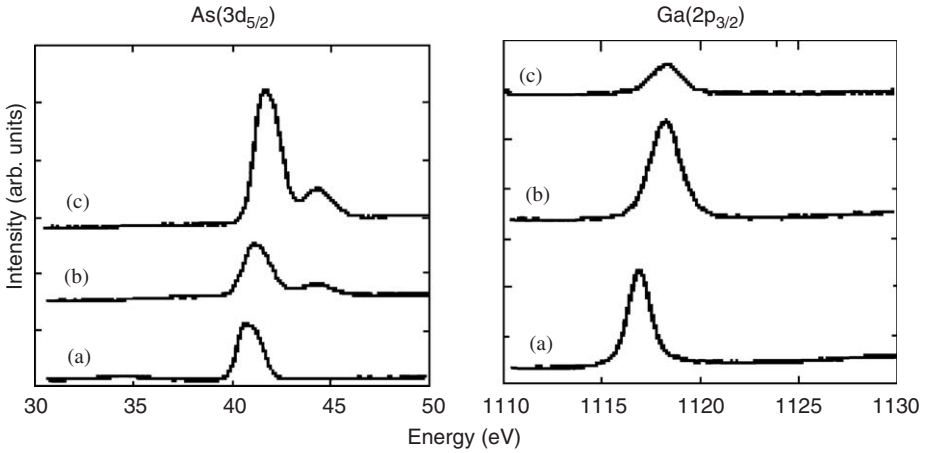

Fig. 3. XPS spectra of GaAs films deposited on titanium at different duty cycles (a) 50%, (b) 25% and (c) 10%.

various duty cycles is due to the variation of crystallite size with duty cycle. In an earlier work on CdSe, it was found that the band gap of CdSe varied from 1.725 to 2.40 eV on varying the electro-deposition parameters. Strong and weak confinements were noticed for the films. The effective Bohr radius for CdSe is 27 Å. For strong confinement, the exciton energy is given by

$$E_s = E_g + h^2\pi^2/2\mu^2 - 1.786e^2/4\pi\varepsilon_0\varepsilon R - 0.248E^*_{Ry}$$

where E_g is the band gap of bulk CdSe, the first term is related to the quantum localization energy, the second term represents the Coloumb energy and the third term represents the correlation energy in which E^*_{Ry} is the effective Rydberg energy and can be written as

$$\{\mu e^4/2(4\pi\varepsilon_0\varepsilon)^2h^2\}$$

where, μ is the reduced effective mass, ε is the dielectric constant for CdSe and ε_0 is the permittivity of free space. The results observed in this investigation may be explained on a similar basis.

Fig. 3 shows high resolution XPS spectra of the Ga($2p_{3/2}$) and As($3d_{5/2}$) core levels of the films deposited at three different duty cycles. Scan (a) indicates the XPS spectrum of the GaAs films deposited at a duty cycle of 50%. Scan (b) Indicates the XPS spectrum for the films deposited at a duty cycle of 25% and ScanI indicates the XPS spectrum for the films deposited at a duty cycle of 10%. It is observed for the films deposited at higher duty cycles (greater than 25%) the films are stoichiometric with Ga:As ratio of 1:1, for lower duty cycles a slight excess of Arsenic is observed, this may be due to the fact that Arsenic is more noble compared to gallium and at lower duty cycles, since the ON time is very low, this facilitates the deposition of more Arsenic compared to Gallium.

Raman scattering specta of the GaAs films grown at duty cycles of 50% and 15% are exhibited in Fig. 4. In the case of films deposited at duty cycles higher than 25%, both TO (268 cm^{-1}) and LO (292 cm^{-1}) phonon peaks are clearly seen. This feature further suggests the existence of

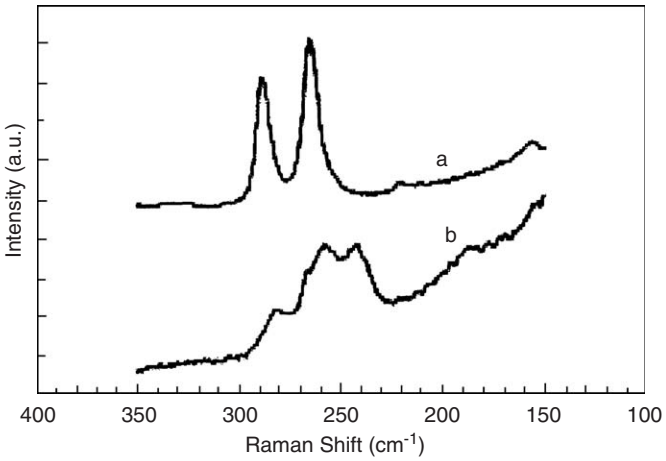

Fig. 4. Raman scattering spectra of GaAs films deposited on titanium at different duty cycles (a) 50% and (b) 15%.

(1 1 1) plane parallel to the substrate surface [17]. In addition, no distinct amorphous GaAs peak, which should be broad and appear at a range of about 200–290 cm^{-1}, is observed in the spectrum [17]. Therefore, crystalline content in the film is considered to be almost 100%. However, in the case of films deposited at duty cycles lower than 25%, the broad feature of the RSS spectrum indicates the presence of amorphous GaAs.

The cross plane resistivity of the films were found to be around $10^5\,\Omega$ cm. Annealing the films in Gallium vapours at 500 °C for 10 min in argon atmosphere reduced the resistivity by two orders of magnitude.

Photoelectrochemical cells were made using the films as photoelectrodes and graphite as counter electrode in 1 M polysulphide electrolyte. At 60 mW cm^{-2} illumination, an open circuit voltage of 0.6 V and a short circuit current density of 5.0 mA cm^{-2} were observed for the films deposited at a duty cycle of 50%. Fig. 5 shows the load characteristics of GaAs films deposited at a duty cycle of 50% and at different intensities. Both open circuit voltage

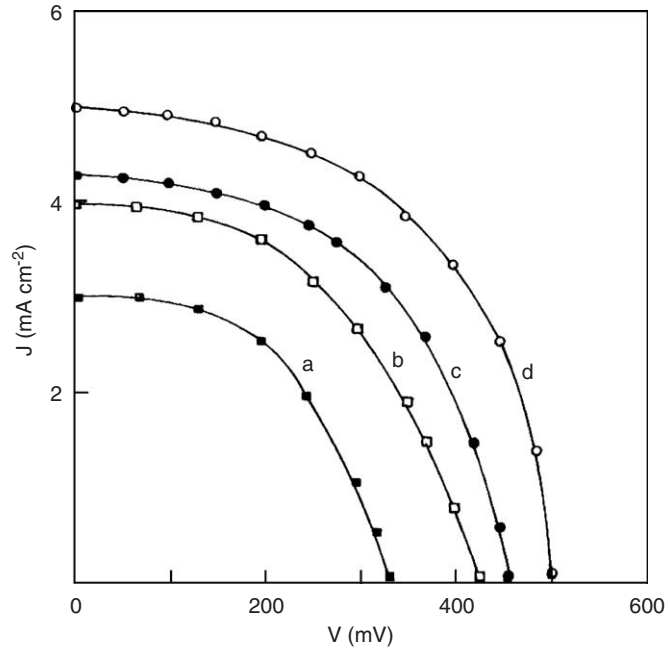

Fig. 5. Load characteristics of GaAs films deposited on titanium at a duty cycle of 50% and at different intensities (a) 20 mW cm^{-2}, (b) 30 mW cm^{-2}, (c) 50 mW cm^{-2}, (d) 60 mW cm^{-2}.

and short circuit current are found to increase with intensity. The ideality factor calculated from the $\ln J_{sc}$ vs V_{oc} plot indicates an ideality factor of 2.1 and a reverse saturation current density of 10^{-7} A cm^{-2}. The values of the current and voltage are lower than those obtained with single crystal GaAs electrodes [18,19], but they are higher than the values obtained with thin film electrodes [20,21].

4. Conclusion

The results indicate that GaAs films of device quality can be easily prepared by the pulse plating technique. Moreover, the method can be scaled up to large areas for solar cell fabrication.

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