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Properties of GaAs films deposited by pulse periodic technique

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Abstract GaAs is a III-V compound possessing high mobility and a direct band gap of 1.43 eV , making it a very suitable candidate for photovoltaic applications. Thin GaAs films were prepared at room temperature by plating an aqueous solution containing $GaCl_3$ and As_2O_3 at a pH of 2. The current density was kept as 50 mA cm^{-2} and the duty cycle was varied in the range 10–50%. The films were deposited on titanium 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. The surface roughness of the films varied from 3 nm to 6 nm as the duty cycle increased. Raman spectra indicated both the LO and TO phonons for the films deposited at duty cycles above 25%. Photoelectrochemical studies indicated that the current and voltage output are higher than earlier reports on thin film electrodes.

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. 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. 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 [3], 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.

The pulse plating technique has advantages over conventional plating technique, in conventional plating either the current or potential can be varied. In the pulse plating technique, current, potential or duty cycle can be varied. Duty cycle is defined as the ratio of the ON time (duration for which the current/voltage is applied) to the total time(ON time plus the OFF time).

$$\text{Duty cycle} = \text{ON time} + (\text{ON time} + \text{OFF time})$$

During the OFF time (duration during which no current/potential is applied), improperly formed nuclei and adsorbed species will get desorbed from the deposit. Thus the quality of the deposit obtained by

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pulse plating would be better than with conventional plating.

Experimental methods

Thin GaAs films were prepared at room temperature by plating an aqueous solution containing $GaCl_3$ and As_2O_3 at a pH of 2. 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 and tin oxide coated glass substrates. Films were deposited on conducting glass substrates for optical absorption studies. The plating time was 20 min. Thickness of the films estimated by gravimetry was 2.0 μm. The films were characterized by X-ray diffraction technique. Films exhibited polycrystalline nature with peaks corresponding to single phase GaAs. The intensity of the peaks was 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.

Results and discussion

Figure 1 shows the X-ray diffraction results obtained from films deposited at different duty cycles on titanium substrates. The XRD patterns of the films deposited on conducting glass were similar to the ones on titanium substrates. Hence results are presented for the films deposited on titanium substrates. 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). The crystallite size was evaluated by using the Debye–Scherrer equation [4]:

$$\text{Crystallite size} = 0.9\lambda/(\beta\cos\theta)$$

where β is the full width half maximum, θ is the diffraction angle λ is the wavelength of CuKα radiation. The crystallite size was roughly in the range 50–70 Å in size for higher duty cycles ranging from 25% to 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 on pulse plated CdSe films [5]. According to Moss [6], the optical band gap 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 transmittance measurements. The plot of photon energy, $h\nu$ (h—Plank constant, ν—frequency), versus the square of absorption coefficient, α^2, as shown in Fig. 2, extrapolation of the linear region to the energy axis yielded a band gap of 1.40 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% to 50%, the

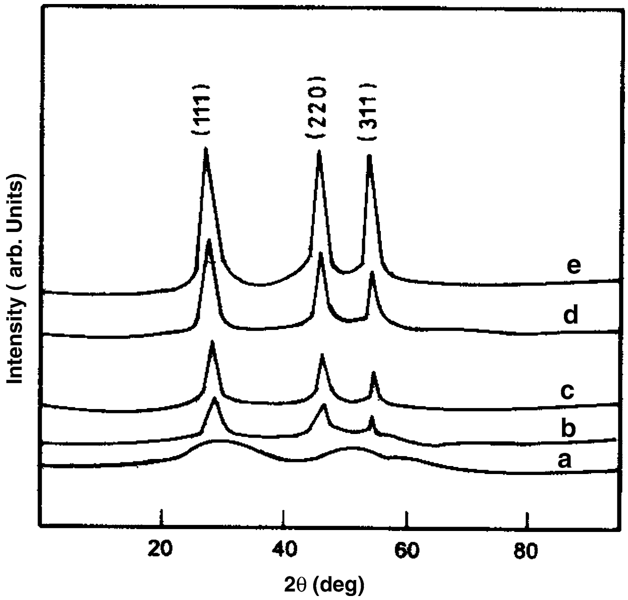

Fig. 1 X-ray diffraction pattern of GaAs films deposited at different duty cycles (a) 10% (b) 15% (c) 25% (d) 35% (e) 50%

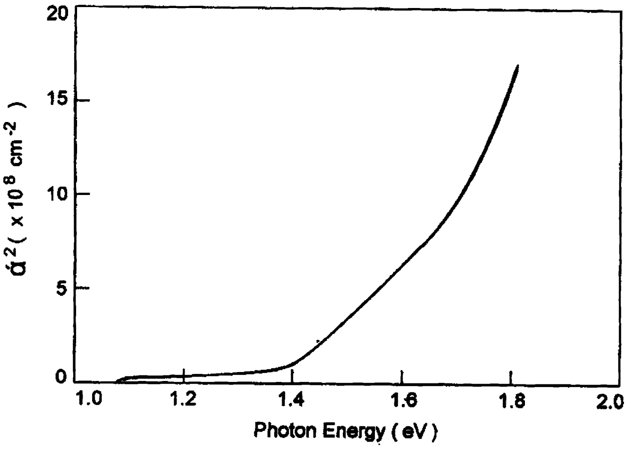

Fig. 2 $(\alpha)^2$ vs. hν plot for the GaAs films deposited at a duty cycle of 50%

Table 1 Variation of crystallite size with duty cycle

Duty cycle (%)	Crystallite size (nm)
10	1.5
20	3.0
30	5.5
40	6.3
50	7.0

band gap value decreases from 2.02 eV to 1.40 eV. This is due to the decrease in particle size with decrease of duty cycle. The variation of band gap at 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

$$\left\{\mu e^4/2(4\pi\varepsilon 0\varepsilon)^2 h^2\right\}$$

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 Scan (c) 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 (>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.

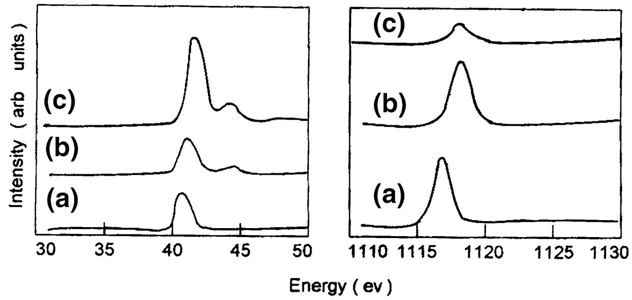

Fig. 3 XPS spectra of GaAs films deposited at different duty cycles (a) 50% (b) 25% and (c) 10%

Atomic force micrographs of GaAs films deposited at different duty cycles is shown in Fig. 4. As the duty cycle increases, the crystallite size also increases. The crystallite size changes from 40 Å to 100 Å as the duty cycle increases. The surface roughness is found to increase from 3 nm to 6 nm as the duty cycle increases from 10% to 50%.

Raman scattering spectra of the GaAs films grown at duty cycles of 50% and 15% are exhibited in Fig. 5. In the case of films deposited at duty cycles higher than 25%, both TO (268 cm^{-1}) and LO (292 cm^{-1}) phonon

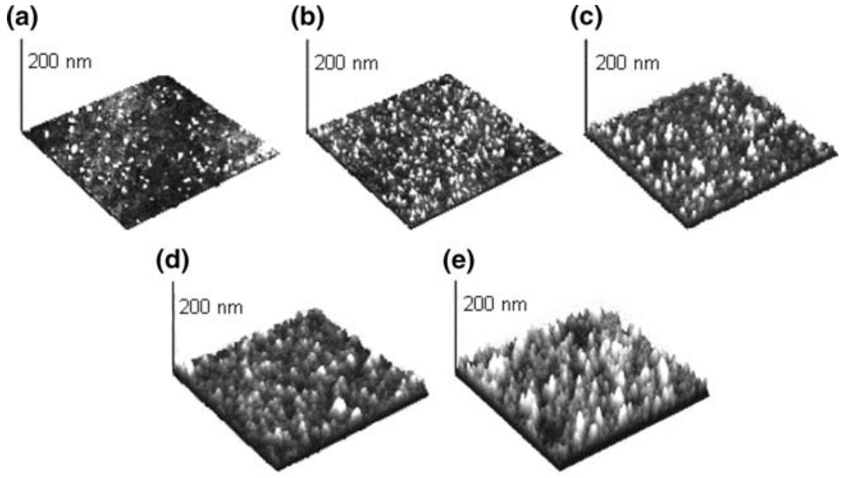

Fig. 4 Atomic force micrographs of GaAs films deposited at different duty cycles (a) 10% (b) 15% (c) 25% (d) 35% (e) 50%

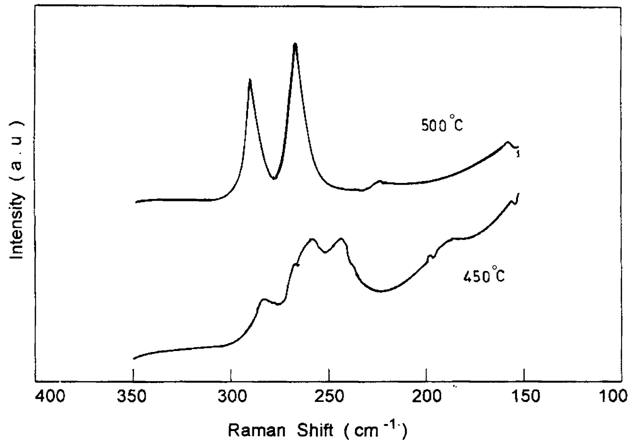

Fig. 5 Raman scattering spectra of GaAs films deposited at different duty cycles (a) 50% and (b) 15%

peaks are clearly seen. This feature further suggests the existence of (1 1 1) plane parallel to the substrate surface [7]. 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 [7]. 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 105 ohm cm. Annealing the films in Gallium vapours at 500°C for 10 min in argon atmosphere reduced the resistivity by two orders of magnitude.

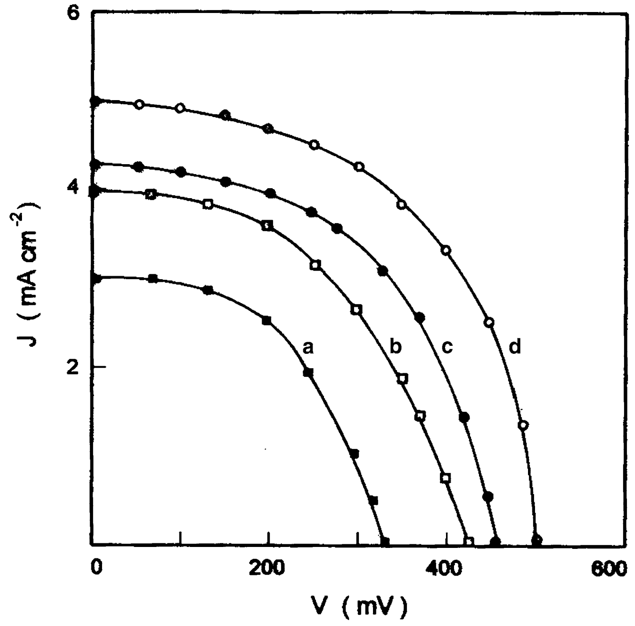

Fig. 6 Load characteristics of GaAs films deposited at a duty cycle of 50% and at different intrensities (a) 20 mW cm^{-2} (b) 30 mW cm^{-2} (c) 50 mW cm^{-2} (d) 60 mW cm^{-2}

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. 6 shows the load characteristics of GaAs films deposited at a duty cycle of 50% and at different intensities. Both open circuit voltage 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 [8, 9], but they are higher than the values obtained with thin film electrodes [10, 11].

Conclusion

The results indicate that nanocrystalline GaAs films could easily prepared by the pulse plating technique. Very fine grain films of the order of 5–10 nm can be deposited by this technique.

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