

Preparation and characterization of pulse electrodeposited GaAs films

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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 by plating an aqueous solution containing GaCl₃ and As₂O₃ at a pH of 2 and at room temperature. The current density was kept at 50 mA cm⁻² and 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. Atomic force microscope measurements indicated uniform coverage with large crystallites for the films deposited at higher duty cycles. 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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1 Introduction

GaAs is one of the technologically important III–V semiconductors useful for optoelectronic and photovoltaic applications. Several techniques like flash evaporation [1], Vapor Phase Epitaxy (VPE) [2], Molecular Beam Epitaxy (MBE) [3], chemical beam epitaxy [4], spray pyrolysis [5], sputtering [6–10], and pulsed laser ablation [11] 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 [12], a systematic study of the effect of the 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 GaCl₃ and As₂O₃ at a pH of 2 and at room temperature. The current density was kept at 50 mA cm⁻² and the duty cycle was varied in the range 10–50%. The films were deposited on titanium, nickel and tin oxide coated glass substrates. The plating time was 20 min. Thickness of the films estimated by gravimetry was 2.0 μm. The films were characterized by an X-ray diffraction technique. The 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. Scanning Electron Microscopy (SEM) studies indicated that the

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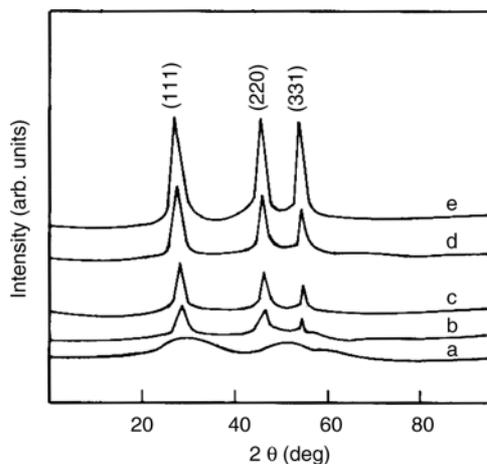


Fig. 1 X-ray diffraction patterns of GaAs films deposited at different duty cycles. (a) 10%, (b) 15%, (c) 25%, (d) 35%, (e) 50%.

grain size decreased with current density. Laser Raman studies were carried out on the films using a Renishaw LABRAM laser Raman spectrometer. X-ray Photoelectron Spectroscopy (XPS) studies were made using a VG ESCALAB MKII spectrometer with Mg K_{α} radiation.

3 Results and discussion

Figure 1 shows the X-ray diffraction results obtained from films which were deposited at different duty cycles. 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 Debye–Scherrer equation indicates that the diffraction comes from GaAs crystallites of roughly 70 Å in size for higher duty cycles ranging from 25% to 50%. The films grown with duty cycles of 10% and 15% also show 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 in work on pulse plated CdSe films [13].

According to Moss et al. [14], the optical band gap of a direct-gap semiconductor material can be deduced from the linear relation between the square of the 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, $h\nu$ (h : Planck constant, ν : frequency), versus the square of the absorption coefficient, α^2 , as shown in Fig. 2, indicates that the band gap (x -intercept) of the film is about 1.4 eV for the films deposited at a duty cycle of 50%. This

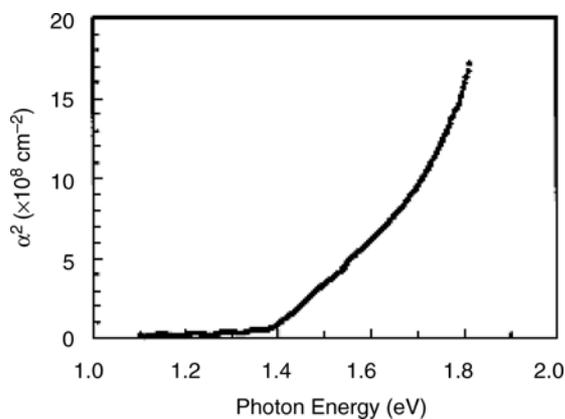


Fig. 2 α^2 versus $h\nu$ plot for the GaAs films deposited at a duty cycle of 50%.

Table 1 Variation of band gap with duty cycle.

duty cycle (%)	band gap (eV)
10	2.02
25	1.86
40	1.63
50	1.40

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 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 the 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 eV to 2.40 eV on varying the electrodeposition parameters. Strong and weak confinements were noticed for the films. The effective Bohr radius for CdSe is 27 angstroms. For strong confinement, the exciton energy is given by

$$E_s = E_g + h^2 \pi^2 / 2\mu^2 - 1.786 e^2 / 4\pi\epsilon_0\epsilon R - 0.248 E_{Ry}^*$$

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

$$\mu e^4 / 2(4\pi\epsilon_0\epsilon)^2 h^2,$$

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.

Figure 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 that the films deposited at higher duty cycles (greater than 25%) are stoichiometric with a 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.

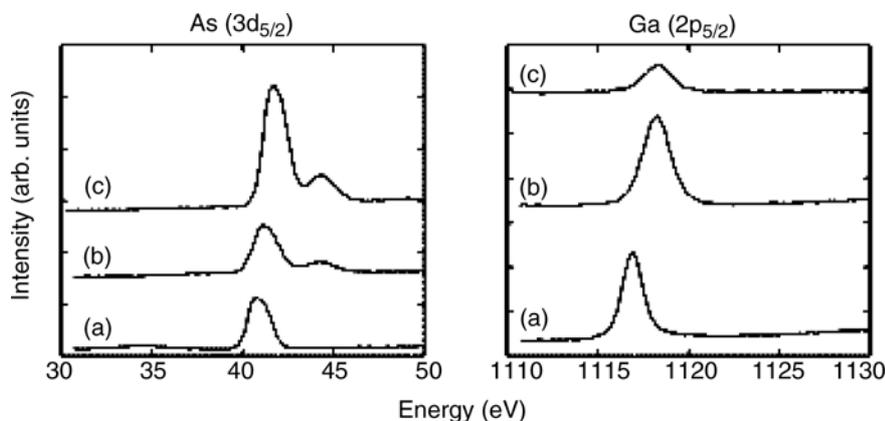


Fig. 3 XPS spectra of GaAs films deposited at different duty cycles. (a) 50%, (b) 25%, (c) 10%.

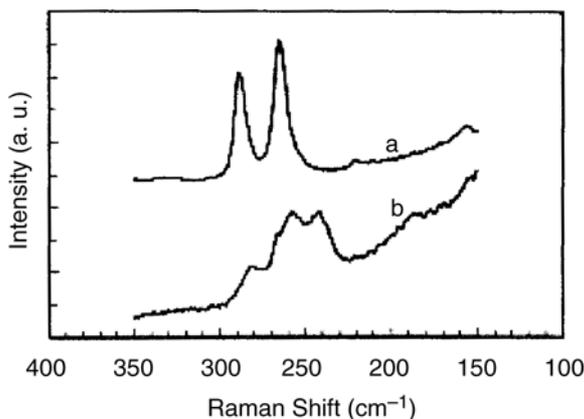


Fig. 4 Raman scattering spectra of GaAs films deposited at different duty cycles (a) 50%, (b) 15%.

Raman scattering spectra (RSS) 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 a (111) plane parallel to the substrate surface [15]. In addition, no distinct amorphous GaAs peak, which should be broad and appear at a range of about $200\text{--}290\text{ cm}^{-1}$, is observed in the spectrum [15]. 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 was found to be around $10^5\ \Omega\text{ cm}$. Annealing the films in gallium vapors at $500\text{ }^\circ\text{C}$ for 10 min in argon atmosphere reduced the resistivity by two orders of magnitude.

4 Conclusion

The results indicate that GaAs films can be easily prepared by the pulse plating technique for optoelectronic device applications. Moreover, the method can be scaled up to deposit large-area thin films.

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