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Laser alloyed tin layers on GaAs

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A Q-switched ruby laser has been used to alloy deposited layers of tin on (100) GaAs. The tin concentration in the GaAs substrates has been investigated by electrical measurements, electron probe microanalysis, Rutherford backscattering and transmission electron microscopy. The results show that a high concentration of tin diffuses into the GaAs for an energy density up to 0.6 J cm^{-2} and the electrical properties improve with increasing energy density. However, at high energy densities this leads to the introduction of damage near the GaAs surface. At the highest energy density of 2 J cm^{-2}, very complex dislocation networks are produced and a cellular structure results along with microcracking of the surface. This produces high levels of residual strain in the surface.

1. Introduction

There are several advantages to be obtained from forming ohmic contacts to semiconductors by laser alloying deposited metals rather than using the furnace treatment that is common throughout industry. In the former case only a thin surface layer is heated and the temperatures attained may increase the solubility of the dopant and hence give rise to a lower contact resistivity than is possible using a furnace. Laser alloying has recently been shown to produce good ohmic contacts from Au/Ge layers on n-type GaAs [1–3] and low values of contact resistivity were obtained with good surface morphology. The formation of p$^+$ layers by laser alloying magnesium [4] and zinc [5] layers on GaAs has also been successful producing a hole concentration in excess of 1×10^{21} cm^{-3} in the case of zinc, which is the highest hole concentration recorded for zinc in GaAs. Because of this success, which we believe is due to interdiffusion in a thin molten surface layer followed by a very fast quench to ambient we began a study of deposited tin layers in an attempt to obtain similarly high carrier concentrations. Tin was chosen because it is a useful donor atom in GaAs, its diffusion is amenable to analysis by Rutherford backscattering, it is readily detected by the electron microprobe and it can be etched off to reveal the interface for optical and transmission electron microscopy. Our initial results concerning the metallurgy of the tin–GaAs following laser annealing have been published already [6]. In this paper we present results of a detailed study of the laser alloying of tin layers on GaAs and explain how the results from the various measurement techniques used correlate with one another.

2. Method

Bulk (100), semi-insulating GaAs wafers were cut into 4 mm × 4 mm square samples. The dice were degreased in organic solvents and boiled in concentrated HCl for a few minutes before being loaded into the vacuum system. At a background pressure of 3×10^{-6} torr, 50 nm of tin was deposited on to the GaAs surface, the thickness being measured with a calibrated quartz crystal monitor. The samples were irradiated in air with a single pulse from a Q-switched ruby laser. Both homogenized [6] (6 mm diameter) and non-homogenized (8 mm diameter) beams were employed. The former produced a spatially uniform energy density equal to the total energy incident on the sample divided by the beam cross-sectional area. However, the energy density of the latter was approximately Gaussian in cross-section. In this case the sample was placed at the centre of the beam where the energy was the most uniform and the incident energy density was estimated by dividing the total energy in the central 4 mm diameter part by its area. Although the magnitude of the energy density

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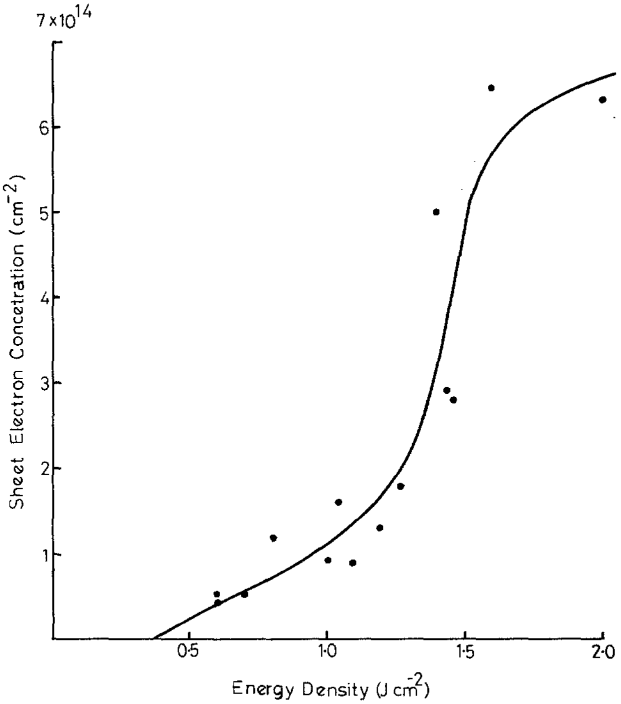

Figure 1 Sheet electron concentration as a function of energy density.

estimated for the non-homogenized beam was more uncertain than for the homogenized beam, results for the two types of irradiation were very similar. After irradiation with energy densities in the range 0.1 to 2.0 J cm^{-2}, the residual tin on the surface of the GaAs was removed by boiling in concentrated HCl for 15 min.

Rutherford backscattering (RBS) of a 1 mm diameter beam of 1.5 MeV He$^+$ ions was used to estimate the quantity of tin which had diffused into the GaAs as a result of the laser irradiation. This technique was used also to evaluate the degree of crystalline perfection at various stages of the experiments. For this, the damage parameter, $X_{\min}$, which is the ratio of the yields behind the surface peaks in the aligned and random spectra respectively, was measured. The sheet electron concentration and electron concentration profiles were measured on the laser alloyed samples using the Van der Pauw technique together with chemical etching. Since Rutherford backscattering is sensitive to the presence of tin only within about 0.1 μm from the surface of the GaAs, the total amount of tin within the GaAs was estimated using a JEOL JXA-50A microprobe X-ray analyser. For this experiment, the electron beam was kept stationary so that a small volume (about 1 μm^3) could be analysed for a time of 100 sec. In this way the signal-to-noise ratio was improved. The results are the mean of at least six determinations of tin concentration on different parts of a specimen.

The tin–GaAs interfaces, examined by transmission electron microscopy (TEM), were prepared from 2 mm x 2 mm squares of GaAs treated in the same way as described above. The surface to be examined was protected with Lacomit and specimens were thinned chemically on a rotating stage from the back untreated side. 10% bromine in methanol was used as a thinning agent to produce a thin foil containing the interface. A JEOL TEMSCAN 200CX was used to examine the specimens.

3. Results

3.1. Electrical measurements

Electrical measurements were performed on samples following the removal of residual tin which had not diffused into the GaAs. The sheet electron concentration was found to increase with increasing energy density as shown in Fig. 1. In accordance with these results, both the penetration depth of the electrically active tin and the peak electron concentration increased with increasing energy density (Fig. 2). That is as the energy density increased, the variation of the electron concentration with depth changed from a narrow peak to a diffusion-like profile. The maximum electron concentration was about 6 x 10^{19} cm^{-3}.

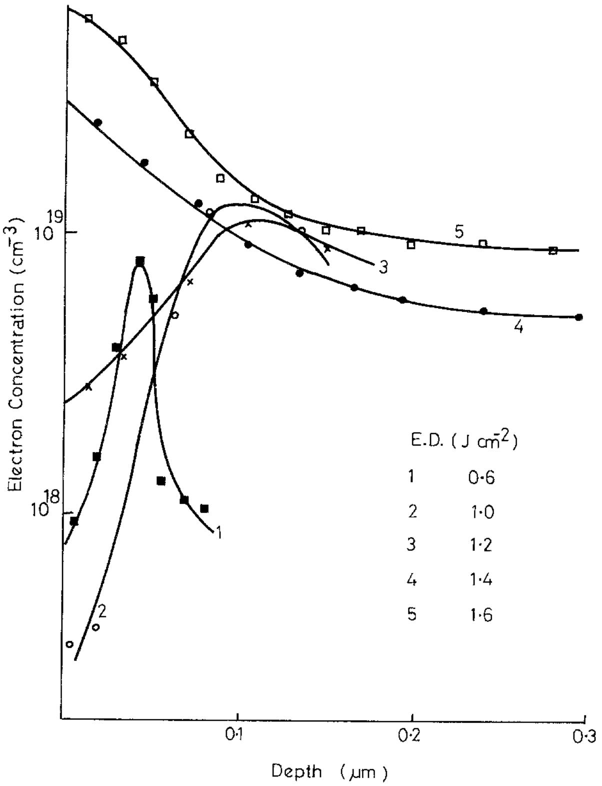

Figure 2 Electron concentration profiles as a function of energy density.

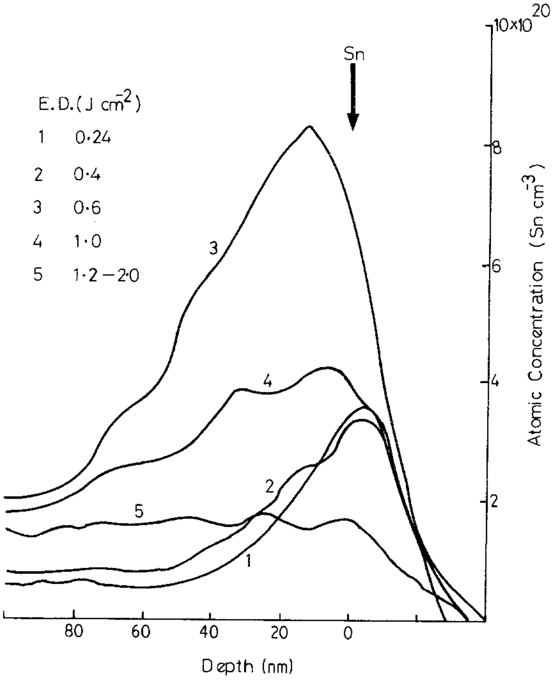

Figure 3 Tin concentration profiles as a function of energy density obtained from Rutherford backscattering spectra following removal of residual tin from the surface.

3.2. Rutherford backscattering

These measurements were performed on samples following the removal of residual tin. Fig. 3 shows the indiffused tin concentration profiles in the GaAs following laser irradiation. For energy densities up to 0.4 J cm^{-2}, there is a relatively high concentration of tin (3 to 4 $\times$ 10^{20} atoms cm^{-3}) near the surface and the profiles appear not to change significantly with energy density. Following an irradiation at 0.6 J cm^{-2}, a large concentration of tin diffused into the GaAs with a peak value of about 8 $\times$ 10^{20} atoms cm^{-3}. At higher energy densities, the peak value decreases reaching an approximately constant value of almost 2 $\times$ 10^{20} atoms cm^{-3} for energy densities above 1.2 J cm^{-2}. Note that the apparent concentration of tin above the surface of the GaAs is an artefact and is the result of the finite resolution of the surface barrier detector used to monitor the energy of the backscattering helium particles.

The backscattering yield from the GaAs was also recorded and from these spectra the damage parameter, $X_{\min}$, was deduced (Fig. 4). The magnitude of $X_{\min}$ was found to increase with increas-

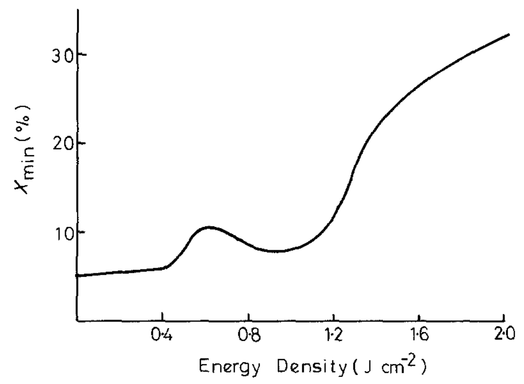

Figure 4 Damage parameter, X_{min}, as a function of energy density after removal of residual tin.

ing energy density, although there is a peak occurring at about 0.6 J cm^{-2} whose relevance will be discussed later. At energy densities less than or equal to 0.4 J cm^{-2}, X_{min} is about 5.0% and equals the value for good crystalline GaAs. Thus the GaAs is not significantly affected until irradiation is carried out above 1 J cm^{-2} when it becomes severely damaged.

3.3. Electron microprobe analysis

Before removing the residual tin it was found that very little tin was lost following irradiation up to about 0.5 J cm^{-2}. However, above 0.5 J cm^{-2}, the total tin remaining on or within the surface of the GaAs reduced with increasing energy density. Thus, tin was lost from the samples [7]. Samples which were analysed following the removal of tin were measured using the spot mode of operation, i.e. an unscanned electron beam. In this way, it was possible to determine the total concentration of tin which had diffused into the GaAs (Fig. 5) since the X-rays probed to about 1 μm depth and the melt depth or the maximum diffusion depth of tin is estimated to be less than 1 μm [8] for an energy density of 2 J cm^{-2}. Thus Fig. 5 indicates the relative concentration of indiffused tin as a function of energy density.

3.4. Transmission electron microscopy

Following the removal of the residual tin, the samples were thinned for TEM analysis. Figs. 6a to e illustrate the results obtained as a function of energy density. At energy densities below 0.6 J cm^{-2} (Figs. 6a and b) the GaAs is single crystal with no extra diffraction spots, but there are linear bands of contrast running parallel to each other which may be due to precipitates. The surface of the GaAs also becomes noticeably rough compared with irradiation below 0.6 J cm^{-2} when the energy density is increased. At about 1.0 J cm^{-2}, the surface becomes very rough, the GaAs is still single crystal with no extra diffraction spots but the specimen shows comparatively uniform background contrast with a few irregularities which may be due to the presence of tin precipitates (Fig. 6c). However, following irradiation at 1.5 J cm^{-2}, many dislocations are introduced which generate a cellular structure (Fig. 6d) but the GaAs is still a single crystal. At the highest energy density of 2 J cm^{-2}, there is a large density of dislocation cells (Fig. 6e) and surface cracks generating a typical fringe contrast. As a result of this, the exposed interface is found to be under a very high level of residual strain and there is a large variation of the diffraction conditions across the

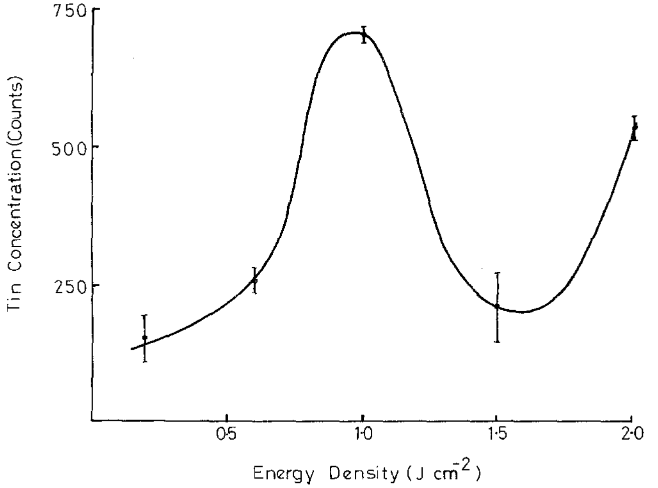

Figure 5 Total concentration of tin as a function of energy density obtained from electron microprobe analysis.

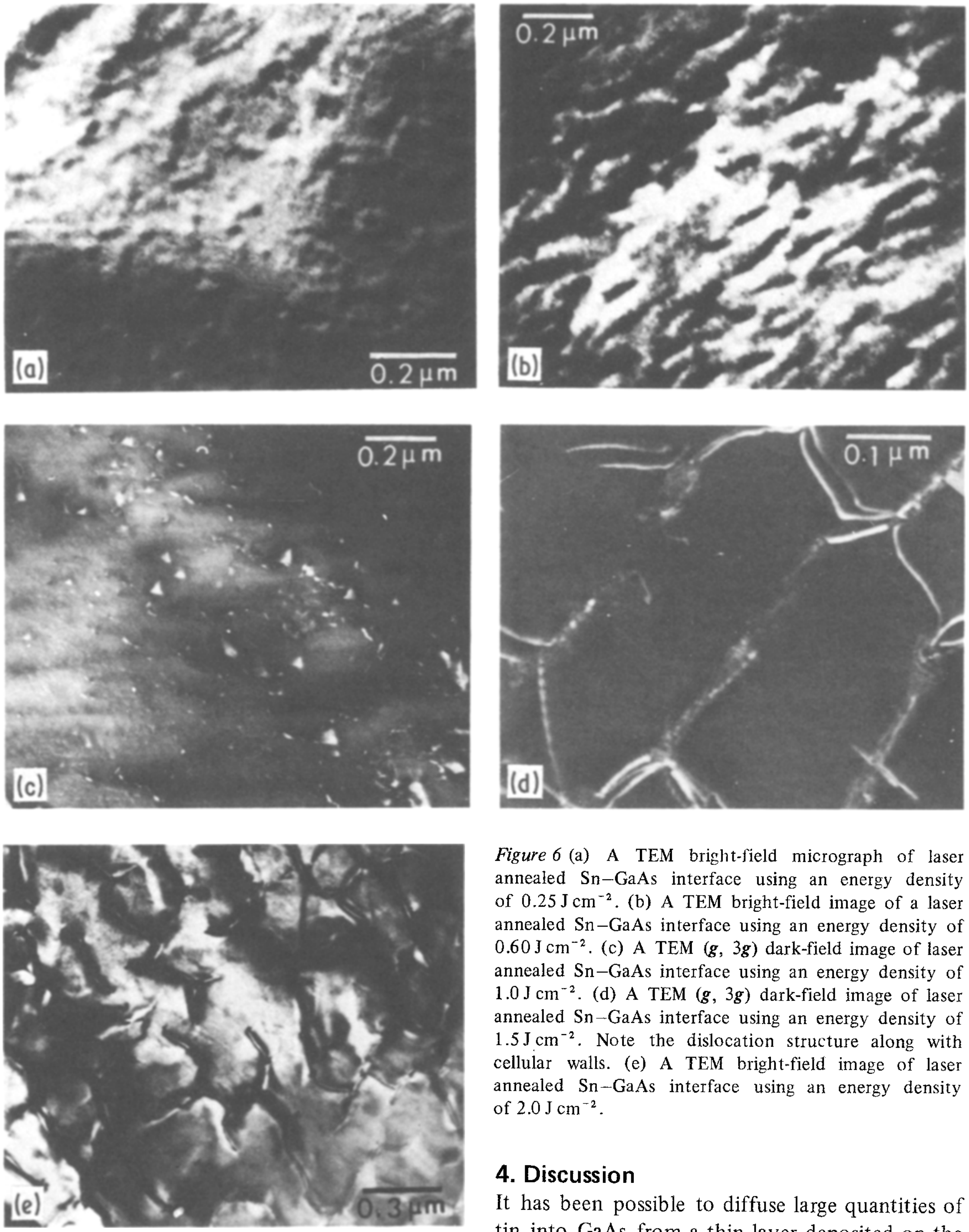

Figure 6 (a) A TEM bright-field micrograph of laser annealed Sn–GaAs interface using an energy density of 0.25 J cm^{-2}. (b) A TEM bright-field image of a laser annealed Sn–GaAs interface using an energy density of 0.60 J cm^{-2}. (c) A TEM (***g***, 3***g***) dark-field image of laser annealed Sn–GaAs interface using an energy density of 1.0 J cm^{-2}. (d) A TEM (***g***, 3***g***) dark-field image of laser annealed Sn–GaAs interface using an energy density of 1.5 J cm^{-2}. Note the dislocation structure along with cellular walls. (e) A TEM bright-field image of laser annealed Sn–GaAs interface using an energy density of 2.0 J cm^{-2}.

micrographs. We believe the dislocation networks which were found to consist of closely lying dipoles and multipoles, contain precipitates (Fig. 6d). Also the size of the cells becomes smaller as the energy density was raised above 1 J cm^{-2}.

4. Discussion

It has been possible to diffuse large quantities of tin into GaAs from a thin layer deposited on the surface by irradiating with single pulses from a Q-switched laser. The indiffused tin concentration has been deduced from both Rutherford backscattering spectra and from X-ray microprobe analysis (Figs. 3 and 5). The RBS results suggest that the concentration of tin within the GaAs is a maximum following an anneal at 0.6 J cm^{-2}

whereas the microprobe indicates that a maximum concentration occurs in the neighbourhood of $1\,\mathrm{J\,cm^{-2}}$. These results are not inconsistent since the RBS data applies to depths up to $0.1\,\mu$m from the surface (Fig. 3) and the microprobe is sensitive to depths of up to $1\,\mu$m. We can conclude, therefore, that following irradiation at an energy density of $1\,\mathrm{J\,cm^{-2}}$, tin diffuses to a depth much greater than $0.1\,\mu$m. The total tin concentration at energy densities of about $1.5\,\mathrm{J\,cm^{-2}}$ (Fig. 5) is thought to be due predominantly to segregation of the indiffused tin back to the surface of the GaAs where it precipitates and is subsequently removed by etching in HCl. That is, for energy densities up to about $1\,\mathrm{J\,cm^{-2}}$, the total indiffused tin concentration increases due to increasing penetration of the melt front and this increased melt time. At higher energy densities, the melt front returns to the surface more slowly and hence segregation of tin is more likely to occur [9]. Thus, much of the indiffused tin is returned to the surface where it precipitates and is removed together with the undiffused tin. From Fig. 3, the equilibrium atomic concentration of tin in the melt is about 1.5×10^{20} atoms cm^{-3} (curve 5) which is thus the solubility of tin at the melting point of GaAs. Any diffused tin above this concentration will be swept towards the surface if the melt front is moving sufficiently slowly and this occurs only at higher energy densities since the melt front velocity decreases with increasing energy density [4].

By comparing the RBS data (Fig. 3) with electrical profiles (Fig. 1) it is concluded that a small fraction of the indiffused tin is electrically active at a given energy density. For example, at $0.6\,\mathrm{J\,cm^{-2}}$, the peak atomic concentration is about 8×10^{20} atoms cm^{-3} (Fig. 3) whereas the peak electron concentration is about $8 \times 10^{18}\,\mathrm{cm^{-3}}$ (Fig. 1). However, by comparing channelled and random spectra it was found that more than 70% of the tin atoms reside on lattice sites [7], but clearly not many of these substitutional atoms are measured electrically. The sheet electron concentration saturates above $1.5\,\mathrm{J\,cm^{-2}}$ (Fig. 2) even though the total tin concentration increases between 1.5 and $2.0\,\mathrm{J\,cm^{-2}}$ (Fig. 5). We believe that as the dislocation cell density increases with increasing energy density, more tin is retained in the GaAs than at lower energy densities because it can be trapped in the cell walls rather than be segregated to the external surface. The precipitation in the cell walls gives rise to an increase in total tin concentration within the GaAs and does not affect the tin dissolved in the GaAs which is responsible for the n-type conductivity. Since the cell walls penetrate to at least several 100 nm and possibly through the entire melted region, then RBS will be insensitive to the increase in tin concentration within the walls. That is, the majority of tin detected by the microprobe is at depths greater than $0.1\,\mu$m which is the maximum depth for which RBS is sensitive to tin dissolved in GaAs under our experimental conditions.

The TEM results agree well with the various other experimental data. They suggest that melting of the GaAs probably did not occur below $0.6\,\mathrm{J\,cm^{-2}}$, but at this energy density, the surface becomes rough which is indicative of melting and bands of contrast occur which are thought to be due to the precipitation of tin near the surface. These results are in accord with the very high concentration of tin that has diffused into the GaAs (Fig. 3) of which only a small fraction is electrically active (Fig. 1). Also following an irradiation at $0.6\,\mathrm{J\,cm^{-2}}$, the magnitude of $X_{\min}$ increases to about 10% which is due to the presence of this large concentration of tin. $X_{\min}$ decreases a little at $1.0\,\mathrm{J\,cm^{-2}}$ because of the lower concentration of tin near the surface compared with $0.6\,\mathrm{J\,cm^{-2}}$, but then its magnitude increases monotonically with increasing energy density due to the damage introduced into the GaAs by the laser. This damage is observed in the TEM as due to surface decomposition (roughness) and the introduction of large densities of dislocations.

A previously published paper [10] which studied alloying of tin layers on GaAs by irradiation through the back face with a Nd:glass laser showed that the peak values of 2 to 4×10^{21} tin atoms cm^{-3} occurred within 30 nm of the GaAs surface and about 90% of the tin atoms occupied lattice sites. These values are higher than those reported in this paper; however, the experimental conditions are somewhat different. Nevertheless, results both from the current and from the previous work [5] do follow the same trend.

5. Conclusions

Large quantitites of tin have been diffused into GaAs by laser irradiation of thin deposited layers. The solubility of tin at the melting point of GaAs was estimated as about 2×10^{20} atoms cm^{-3}. Peak electron concentrations up to $6 \times 10^{19}\,\mathrm{cm^{-3}}$ have been recorded which indicate that only part of the total indiffused tin content is electrically active. The best electrical properties occur at energy densities above 1.2 J cm^{-2}. Evidence of precipitate formation was found using transmission electron microscopy and at energy densities above 1 J cm^{-2} dislocation networks formed which eventually gave rise to cracks at the highest energy density of 2 J cm^{-2}. Bearing in mind the different analysis depths of the techniques used, a good correlation was obtained between them.

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