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Optical Characterization of GaAs and GaP Laser-Annealed in High-Pressure Ar Atmosphere

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Pulsed laser annealing was carried out on ion-implanted GaAs and GaP crystals in Ar gas at pressures between 1 and 1000 bar. The laser-annealed specimens were characterized by optical methods such as reflectivity, absorption and photo-acoustic spectroscopy. These methods proved to be sensitive to microscopic crystalline defects and to be capable of characterizing the laser-annealed layer of III-V semiconductors.

§1. Introduction

Laser annealing (LA) is a promising technology in semiconductor processing as a method of restoring surface layers damaged by the implantation of high-energy ions. In silicon, this technique has proved capable of accommodating implanted dopants substitutionally into the crystal lattice even to concentrations high enough to exceed the equilibrium solid solubility. In III-V semiconductors, however, LA has not always proved successful; the resulting electrical activity is often poor and the carrier mobility low. These deficiencies have been attributed to the poor crystallinity caused by the evaporation of group V elements.

Recently, the problem of low electrical activity has been solved by performing pulsed laser annealing in a high-pressure ambient atmosphere, and an electrical activity of 100% and a high mobility close to the theoretically-predicted one were obtained in specimens annealed in an ambient gas at 100 bar without encapsulation.[1)]

The present authors have been working on the characterization of laser-annealed specimens by means of optical reflectivity, optical absorption and photoacoustic spectroscopy, which are known to be non-destructive and contactless means of characterization. The aim of this paper is to show how optical methods are useful for characterizing surface layers laser-annealed in a high-pressure ambient gas.

§2. Experimental

The samples used in the present study were square platelets of area 4×4 mm^2 and thickness 0.3 mm cut from {100} wafers of GaAs and {100} wafers of GaP. Samples of GaAs were implanted with 180 keV Si^+ ions to doses of 1×10^{15} and 5×10^{12} ions/cm^2, while GaP samples were implanted with Te^+ ions at 100 keV. The implanted samples were annealed with a single light pulse of energy 0.65 J/cm^2 and duration 25 ns from a Q-switched ruby laser in Ar at 1 to 1000 bar using an apparatus the details of which have been published elsewhere.[1)] The diameter of the laser-annealed area was typically 2 mm for GaAs and 1 mm for GaP.

The reflectivity spectra of a small area were measured using the specially-designed spectrometer illustrated in Fig. 1 over photon energies from 0.5 to 4 eV. The size of the probe light spot at the sample surface was as small as 0.15×0.5 mm^2. The spectra obtained were calibrated by an evaporated aluminium mirror.

The optical absorption spectra for energies between 0.6 and 3 eV were measured with a Cary type-14 spectrophotometer with an appropriate slit to select the laser-annealed area.

The photoacoustic spectra (PAS) were measured using the photoacoustic cell illustrated in Fig. 2 over the near-infrared wavelength region (0.9–1.6 eV) with a microphone (Brüel and Kjaer model 4148) at a modulation frequency of 33 Hz. The beam focal-spot size on the sample surface was 1×1.5 mm^2.[2)] The cell was designed to be movable in the plane parallel to the sample surface with the use of a mechanical stage.

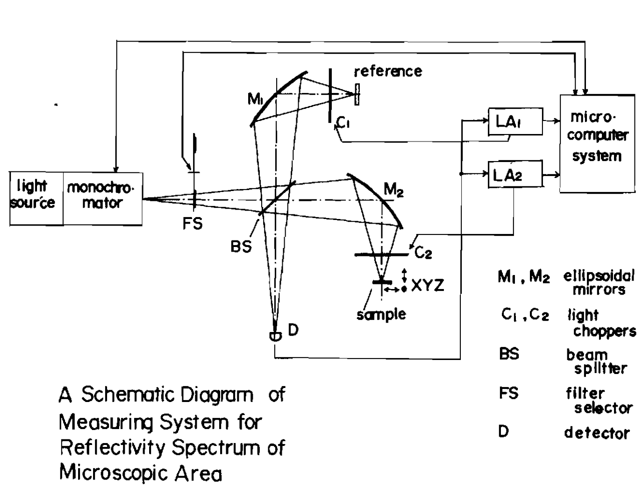

Fig. 1. Schematic diagram of reflectance spectrometer used in this study. MC: monochromator, F: filter, Bs: beam-splitter (double-faced mirror placed in the lower half of the light path), M_1 and M_2: ellipsoidal mirrors, C_1 and C_2: light choppers with rotating sectors with chopping frequencies f_1 and f_2, respectively, D: photodetector, LA_1 and LA_2: lock-in amplifiers.

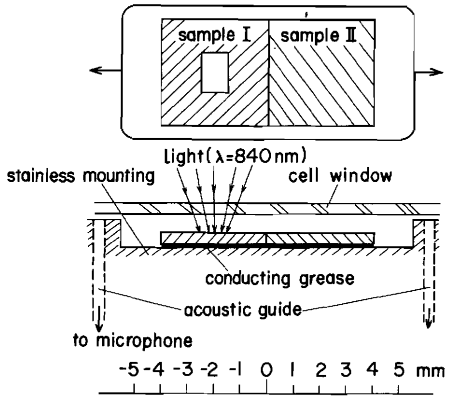

Fig. 2. Photoacoustic cell used in this study.

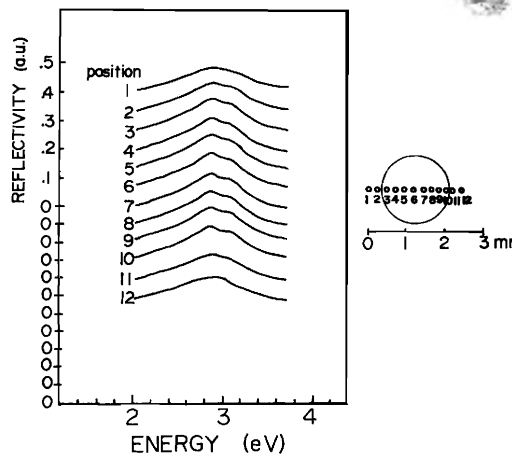

Fig. 4. Reflectivity spectra at various points on the specimen. Curves are arbitrarily shifted for the sake of clarity. Position of probing light spot is shown in the schematical illustration on the right. The large circle denotes the annealed area.

§3. Results and Discussions

3.1 *Reflectivity spectrum of* GaAs

Figure 3 shows the reflectivity spectra of three GaAs specimens—(a) unimplanted, (b) as-implanted with 180 keV Si^+, and (c) laser-annealed in a 100 bar atmosphere. As seen in this figure, the spectrum of an unimplanted sample shows prominent structures around 2.8 and 3.1 eV. These structures are known as peaks E_1 and $E_1+\Delta$, respectively, and have been interpreted as coming from van Hove singularities related to the band structure of this material, i.e. to the crystalline nature of the material.[3]

The structures vanish on implanting with Si^+ ions to doses of 1×10^{15} ions/cm^2. The disappearance of these fine structures has been attributed to the disturbance in the lattice periodicity resulting from the formation of an amorphous layer by high-energy incident ions.[4] The fine structures are restored by irradiation with laser light, as shown by curve (c) in Fig. 3, indicating the recovery of the lattice periodicity. This type of recovery of fine structures has been observed in samples processed by usual furnace annealing.[4]

Figure 4 illustrates the position dependence of the reflectivity spectrum measured by scanning the probing light spot over the sample surface. The spot positions are shown in the left-hand diagram: the large circle denotes the annealed area and the small circles represent the spot position. It is easily seen from Fig. 4 that the spectral shape does not vary very much inside the laser-annealed area, showing that the LA proceeds with considerable uniformity. In addition, the abrupt change in spectral shape on passing through the LA boundary demonstrates the good position selectivity of this method.

In the next place, Fig. 5 shows how the recovery of fine-structures depends upon the ambient conditions under which the LA is performed. Only a slight difference can be observed between curve (a) (annealed under 1 bar air) and curve (b) (1 bar Ar), while fine structures recover to a far greater extent in curve (c) (100 bar Ar) than in the former two. This indicates that the application of higher pressure results in better restoration of the surface crystallinity.

From these results, it is found that we can use the reflectivity spectrum as a convenient means of characterizing a laser-annealed surface. Quick measurements of the reflectivity spectra can be obtained by using an OMA (Optical Multichannel Analyser) system, which should be useful in manufacturing processes.

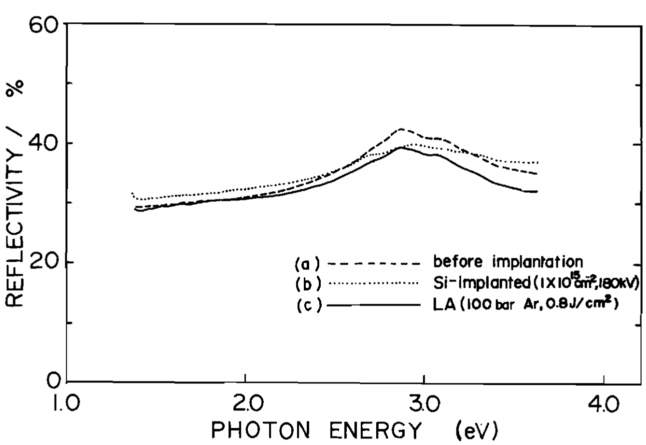

Fig. 3. Reflectivity spectra of (a) unimplanted (dashed curve), (b) as-implanted (dotted curve) and (c) laser-annealed (solid curve) gallium arsenide crystals.

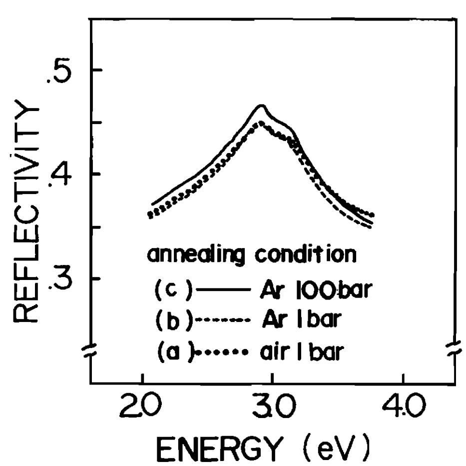

Fig. 5. Reflectivity spectra of three specimens annealed under different conditions; (a) 1 bar air (dotted), (b) 1 bar Ar (dashed) and (c) 100 bar Ar (solid).

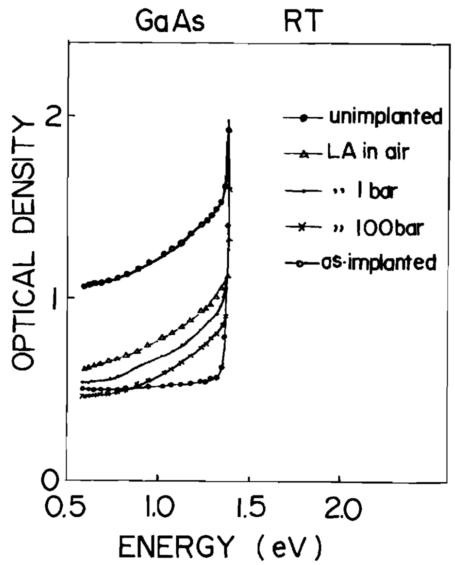

Fig. 6. Absorption spectra of GaAs specimens; (a) unimplanted, (b) as-implanted, (c) annealed in 1 bar air, (d) annealed in 1 bar Ar and (e) annealed in 100 bar Ar.

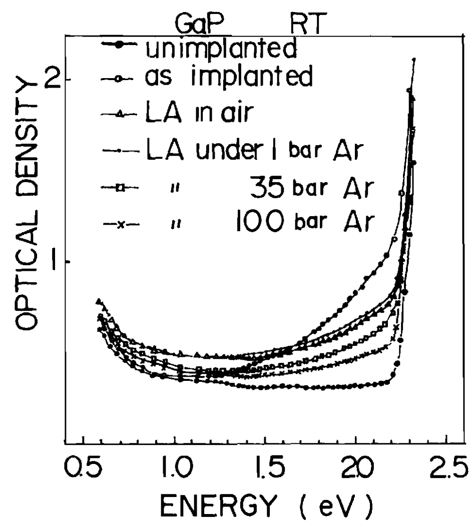

Fig. 7. Absorption spectra of GaP specimens; (a) unimplanted, (b) annealed in 1 bar air, (c) annealed in 1 bar Ar, (d) annealed in 35 bar Ar and (e) annealed in 100 bar Ar.

3.2 *Absorption spectrum of* GaAs *and* GaP

The optical absorption spectra of GaAs and GaP under various annealing conditions are given in Figs. 6 and 7, respectively. The spectra of unimplanted samples and as-implanted ones are also included in these figures for comparison.

In unimplanted semiconductors, sharp absorption edges can be observed in both GaAs and GaP. Ion-implantation introduces strong absorptions below the absorption edge of these crystals, making the specimens opaque. This darkening can be confirmed by inspection in the case of GaP, which has an absorption edge in the visible wavelength range. This implantation-induced absorption may be associated with the formation of an amorphous layer in the surface of the sample due to disturbances in the crystalline structure, caused by high-energy ions. This additional absorption is decreased to a great extent by the laser irradiation.

Recovery of transparency is rather poor for specimens annealed in 1 bar Ar and 1 bar air. An increase in the ambient gas pressure brings about a decrease in the additional absorption, as shown in Figs. 6 and 7. Figure 8 shows the absorption intensities of the tail at 1.38 eV (900 nm) against the ambient Ar pressure for Si-implanted GaAs, while Fig. 9 shows those at 2.21 eV (560 nm) for the Te-implanted GaP specimens.[6] One can see a drastic decrease in absorption on increasing the pressure up to 300 bar, beyond which only a gradual decrease can be observed.

Electrical conduction measurements showed that an ambient gas pressure of 100 bar is sufficient for 100% activity.[1] The optical spectrum, however, indicates that 100 bar is not sufficient for recovery of the crystallinity of the material, but at least 300 bar is necessary. We know from this that the optical characterizations are more sensitive to crystalline properties than the electrical ones.

Let now us consider the origin of the additional absorption. We suspect microscopic crystalline defects to be the cause of the absorption, since SIMS analyses of heavily-implanted GaAs specimens showed that arsenic evaporation takes place in the region near the surface on laser irradiation in 1 bar air or in 1 bar argon ambience, resulting in the formation of vacancies or interstitials. These defects are usually hard to detect by macroscopic measurements such as X-ray or electron beam studies. On the other hand, they can be observed by optical means, since they become light-absorbing or light-scattering centers when decorated by impurity atoms. For the

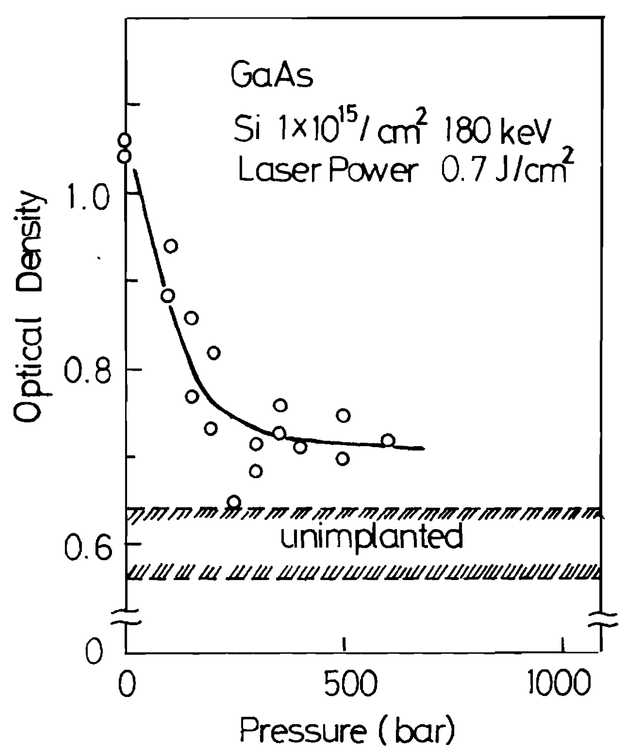

Fig. 8. Dependence of optical absorption intensity (denoted by the optical density) of Si-implanted GaAs at 1.38 eV (900 nm) upon the pressure of the ambient gas. The hatched area shows the range of fluctuation in the optical density of unimplanted specimens.

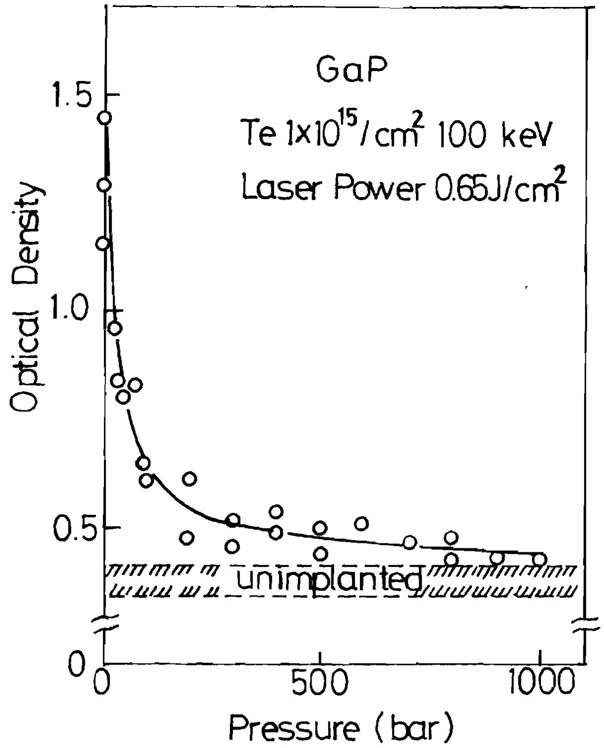

Fig. 9. Dependence of optical absorption intensity of GaP measured at 2.21 eV (560 nm) upon the ambient pressure during laser annealing.

optical applications of III-V semiconductors, incorporation of these centers should be avoided because they are likely to become non-radiative recombination centers.

Next, we explain why the characterization by optical absorption is more sensitive to these defects than that by electrical measurements. Since electrical conduction mainly takes place in the region near the surface, it is insensitive to crystalline defects existing in the region deeper than the activated surface region. On the other hand, absorption measurements involve all the light- absorbing and light-scattering centers residing in the light path.

We also refer to the reason why a high-pressure inert-gas ambient can suppress the absorption tailing. The diffusion length of As or P becomes extremely short when these atoms are mixed with high-pressure Ar gas; the diffusion lengths of As and P in 300 bar argon gas have been calculated as 1/20 of those in 1 bar.[6] They can diffuse a distance of only a few dozen angstroms during the pulse-annealing time of 200 ns. Owing to such small diffusion lengths, a high partial pressure of As or P is built up on the surface, which in turn prevents further evaporation of the group V elements, resulting in suppression of microscopic defects.

3.3 *Photoacoustic spectra*

It is seen in Figs. 8 and 9 that there still remains an absorption tail even for the specimen annealed at the highest pressure in this study. In order to investigate whether the tailing is due to intrinsic defects incorporated by the rapid solidification or due to native effects of dopants at very high concentration, characterization by PAS was carried out for high- and low-dose implanted crystals. Since PAS is essentially an excitation spectrum, it is effective in detecting weak absorption. It is particularly suitable for the characterization of thin film layers and can be applied to low-dose samples whose absorption is too weak to allow its direct measurement.

Figures 10(a) and (b) show the results for 10^{15} and 5×10^{12} cm^{-2} Si^+-implanted specimens, respectively. The laser annealing conditions were left unchanged in the two experiments. From these figures, we find that the remaining absorption tail for a heavily-implanted sample is higher than that for a lightly-implanted one. Therefore, we conclude that the remaining tail should not be attributed to the annealing process but to disturbances inevitably introduced by the incorporation of impurity atoms with extremely high concentration.

§4. Summary

It was first shown that the effects of LA on the crystallinity of ion-implanted gallium arsenides can be monitored by observing the reflectivity spectra around a photon energy of 3 eV. The fine structures around this energy provide a good measure for evaluating the restoration in the lattice periodicity. By measuring reflectivity spectra by scanning with probing light, we can not only distinguish the annealed region from the non-annealed region, but also determine the uniformity inside the annealed area.

Next, it was shown that absorption as well as photoacoustic spectra at photon energies just below the absorption edge are very powerful tools for characterizing LA under a high-pressure ambient gas in GaAs and GaP crystals. These spectra are very sensitive to microscopic defects, which cannot be detected by electrical measurements. It has been shown that an increase in Ar pressure applied during LA improves the transparency at photon energies just below the absorption edge in annealed samples up to a pressure of 300

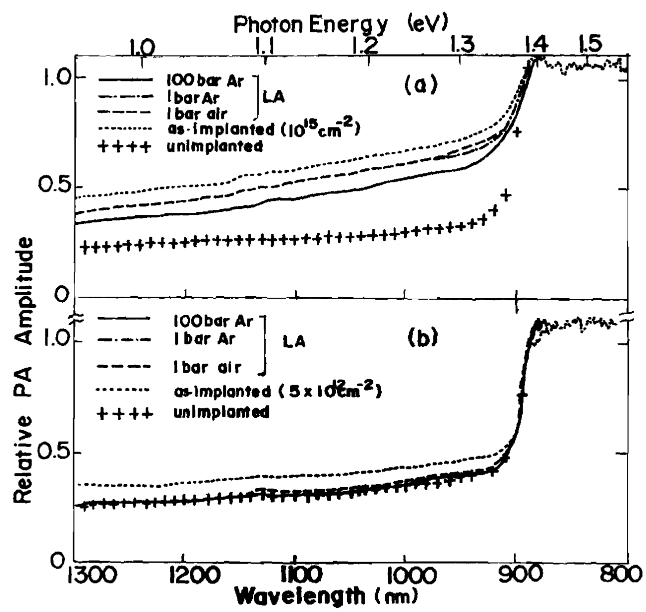

Fig. 10. Photoacoustic spectra of GaAs samples. (a) high-dose implanted specimen (1×10^{15} ions/cm^2) and (b) low-dose implanted specimen (5×10^{12} ions/cm^2).

bars. The additional absorption has been attributed to some kind of microscopic defect decorated by impurity atoms.

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