Pikhtin, A. N.; Airaksinen, V. M.; Lipsanen, H.; Tuomi, T.

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the diffusivity of one species into the other is comparable or larger than its diffusivity in the interfacially growing compound.

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Room-temperature observation of impurity states in bulk GaAs by photoreflectance

A. N. Pikhtin, V. M. Airaksinen, H. Lipsanen, and T. Tuomi
Laboratory of Physics, Helsinki University of Technology, SF-02150 Espoo, Finland

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Photoreflectance (PR) experiments are performed on thick GaAs/GaAs epitaxial layers and on a nearly perfect GaAs single crystal. The first observations of PR spectra induced by impurities (shallow acceptors) in bulk semiconductors like gallium arsenide are reported.

Photoreflectance (PR) spectroscopy has recently been demonstrated as a valuable method for the characterization of compound semiconductors, heterostructures, and multiple-quantum wells (MQW).1,2 Alloy composition, quantum-well width, and interfacial quality of MQW may be controlled by this technique, but practically nothing is known about the possibilities of PR for investigations of impurity states in semiconductors.

A weak peculiarity at long wavelengths in the spectrum of a MQW has been observed recently at a low temperature of compound semiconductors, heterostructures, and demonstrated as a valuable method for the characterization of photoreflectance spectra induced by impurities (shallow acceptors) in bulk semiconductors like gallium arsenide.

The experimental technique for photoreflectance is similar to that discussed in Ref. 5. The modulating beam from an Ar-ion laser (λ = 514 nm) passes through a chopper onto the sample. A monochromatized beam from a tungsten lamp is reflected by the sample at near-normal incidence (about 5°) to a Si detector. The modulated reflectivity spectrum is detected by standard phase-locked techniques. The intensity of the pump beam is from 0.1 to 200 mW/cm².

Two types of samples are used in this study: (1) thick (d ≥ 10 µm) epitaxial GaAs layers grown by vapor-phase epitaxy doped with Te to n = (0.5–2) × 10¹⁷ cm⁻³ on a (100) GaAs substrate and (2) pure undoped (100) GaAs single crystal. The two-crystal x-ray diffraction measurements did not show any inhomogeneities in the single crystal. The half-width of the 400-diffraction peak was less than 17 arcsec. Synchrotron x-ray topographs made at the Hamburger Synchrotronstrahlingslabor did not show any defects, either.

Typical PR spectra for both types of samples are presented in Fig. 1. The classical Franz–Keldysh oscillations are observed in Fig. 1(a) at ω Δ > E_g for an n-type GaAs epilayer with n = 10¹⁷ cm⁻³. The spectrum in Fig. 1(b) (the details of which are presented in Fig. 2, but with higher modulating power) is quite different and more interesting. The very sharp peaks having a half-width of about 6 meV (i.e., less than kT) are seen near the energy gap of GaAs. This part of the spectrum is nearly the same as that of the room-temperature electrolyte-electroreflectance spectrum measured from undoped n-GaAs with a small dc applied bias voltage.6 The main PR peak is observed at the energy of 1.409 eV which is...
smaller than the generally accepted value 1.425 eV for the $E_0$ energy gap of GaAs at 300 K. This difference is probably due to the small amount of indium added to the Ga melt during crystal growth. As can be seen from Fig. 1(b), no Franz–Keldysh oscillations are observed in this specimen. This high-energy part of the spectrum is evidence of the good quality of the material studied.

Considering the long-wavelength part of the spectrum shown in Fig. 2, it is seen that the PR band near $\lambda \approx 900$ nm is evidently due to impurities. When the intensity of the laser light was increased from 0.1 to 200 mW/cm$^2$ the shapes of the fundamental, as well as the impurity peak, changed only a little. The intensity relation of these peaks changed, however, more pronouncedly. With increasing intensity of the laser light the impurity peak increased more than the fundamental one.

Some speculations may be made about the nature of the impurity. At first it is necessary to find its ionization energy. The energy gaps at the critical points of the electron energy-band structure can be found from the maxima and minima of the electroreflectance spectrum.\(^{2,4}\) Using this method we get from Fig. 2 the energy distance of 35 meV. The accuracy of $\pm 2$ meV shown in Fig. 2 corresponds to the spread in experimental data but not to the ionization energy. It is worth noting that the value determined agrees well with the ionization energy of a Si acceptor substituting as an As atom in the GaAs lattice ($E_{\text{Si,As}} = 34.8$ meV).\(^5\) It is well known that silicon is a common impurity in the Czochralski-grown gallium arsenide.

The high-energy side of the impurity peak is slightly distorted. This may be due to a weak transition of about 5 meV above the main impurity transition.

In conclusion, we have reported the first room-temperature observation of photoreflectance due to impurity in bulk gallium arsenide. No Franz–Keldysh oscillations have been observed in undoped high-quality GaAs. The PR signal in the impurity region is anomalously large compared with the intrinsic signal from the fundamental band gap at room temperature. More work is necessary to identify the impurities showing up in the PR spectrum.

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