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Zincblende to diamond structural transition in metastable $(\mathrm{GaAs})_{1-x}$ $(\mathrm{Si}_2)_x$ alloys explained by the linear electro-optic effect

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ABSTRACT. The results obtained from the use of the modulation technique known as reflectance difference spectroscopy (RDS) to detect zincblende to diamond structural transition are shown. The experiments carried out on metastable $(\mathrm{GaAs})_{1-x}$ $(\mathrm{Si}_2)_x$ alloys, (100) oriented and with several silicon concentrations, show that the zincblende to diamond transition occurs for a concentration around $x = 0.37$. This transition is explained on the basis of the linear electro-optic effect.

RESUMEN. Se presentan los resultados obtenidos utilizando la técnica conocida como reflectividad diferencial para detectar transiciones de estructura zincblenda a diamante. Los experimentos realizados en aleaciones metaestables de $(\mathrm{GaAs})_{1-x}$ $(\mathrm{Si}_2)_x$ con orientación (100) y diferentes concentraciones de silicio, demuestran que la transición zincblenda-diamante ocurre a una concentración aproximada de $x = 0.37$. Esta transición se explica con base en el efecto electro-óptico lineal.

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1. INTRODUCTION

Reflectance difference spectroscopy (RDS) is a modulation technique that allows to measure optical anisotropies in the reflectivity of crystals [1, 2]. From the anisotropy spectra we can obtain information about the optical properties of these crystals. RDS was initially developed as a powerful technique to detect surface effects in cubic crystals [3], as in principle, these crystals are isotropic. This last is true for crystals with a diamond structure, such as silicon (Si) and germanium (Ge), but not for crystals with a zincblende structure, such as gallium arsenide (GaAs), where it has been shown that optical anisotropies arising from the bulk of the semiconductor exist [2]. These anisotropies are easily observed. For (100) oriented crystals, depend on the doping concentration and conductivity type of the semiconductor [4]. Therefore, by measuring the optical anisotropies in the bulk of the above semiconductors, we can distinguish between a diamond and a zincblende lattice.

The possibility of a structural transition from zincblende to diamond in metastable $(\mathrm{GaAs})_{1-x}$ $(\mathrm{Si}_2)_x$, $(\mathrm{GaAs})_{1-x}$ $(\mathrm{Ge}_2)_x$ and $(\mathrm{GaSb})_{1-x}$ $(\mathrm{Ge}_2)_x$ alloys when the silicon or germanium concentration is high (about one third of the total concentration), has been proposed before and several experiments have been performed to show this transition[5–9]. One of these experiments consists in the study of the X-ray diffraction patterns of these alloys in order to detect diffraction peaks [7]. Later, RDS was used for this purpose and the structural transition was explained on the basis of local surface effects [9].

In a previous work, the author has shown that semiconductor crystals with a zincblende lattice, (100) oriented, exhibit bulk anisotropies that are related to the linear electro-optic effect [10]. These anisotropies appear as an oscillation around the transition energies E_1 and $E_1 + \Delta_1$, at about 3 eV. The amplitude of this oscillation depends on the doping concentration of the semiconductor and has opposite orientations for n-type and p-type semiconductors. The linear electro-optic effect (Pockels effect) explains this dependence on doping concentration as well as the change in the sign of the oscillation [11]. On the other hand, according to the Pockels effect theory, in semiconductors with a diamond structure, (100) oriented, do not exist anisotropies arising from the bulk of the semiconductor, and therefore such oscillation should not be present in RDS measurements.

In the present work, the transition from zincblende to diamond structure is explained on the basis of the linear electro-optic effect. The measurements of anisotropy spectra for metastable $(\mathrm{GaAs})_{1-x}\,(\mathrm{Si}_2)_x$ alloys with x varying from 0.085 to 0.37 are shown. The results show that for $x = 0.37$, the characteristic oscillation around 3 eV disappears and the spectrum is more similar to that of a diamond structure than to a zincblende one.

2. THEORY

The electro-optic effect is related to the change in the optical properties of a material due to the presence of an electric field [11]. If the material is isotropic, the direction of the electric field is unimportant. However, if the medium is anisotropic, the change in the optical properties will depend on the direction of the field.

The change in the reflectivity of the material is determined by the electro-optic tensor, that for zincblende crystals has the form:

$$\begin{matrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ r_{14} & 0 & 0 \\ 0 & r_{14} & 0 \\ 0 & 0 & r_{14} \end{matrix} \tag{1}$$

where r_{14} is the linear electro-optic coefficient. This coefficient has different values for different zincblende crystals and depends on wavelenght.

In particular, the linear term of the normalized change in reflectivity, due to the presence of an electric field, is given by

$$\Delta R/R = 2(akl + bhl + chk)g(E)E, \tag{2}$$

where a, b and c, are the directional cosines of the electric field and h, k and l, are the directional cosines of the polarization vector of the incident light; $g(E)$ is a function of the photon energy and of the structure of the crystal through r_{14} and E is the magnitud of the electric field.

When an electric field is applied perpendicular to the (100) plane of a zincblende crystal and a light beam is focused also perpendicular to the surface, the expression (2) simplifies to

$$\Delta R/R = 2(hk)g(E)E, \tag{3}$$

since, a and b are equal to zero and c is equal to unity.

The anisotropy in the reflectivity is given by the difference between the reflectivity of the crystal when the light beam is polarized along one symmetry direction of the crystal and when the light beam is polarized along the perpendicular symmetry direction. If we take this difference, the expression (2) is still simpler, becoming:

$$\Delta R/R = -2g(E)E. \tag{4}$$

Equation (4) shows that a linear dependence exists between the amplitude of the anisotropy spectrum (given by $\Delta R/R$) and the magnitude of the electric field E. This electric field appears due to the presence of surface states and it depends on the doping of the semiconductor, being higher for higher doping concentrations [12]. Furthermore, the electric field has opposite direction for n-type semiconductors and for p-type semiconductores and therefore, the anisotropy signal also changes in sign. The term $g(E)$ depends on the wavelength of the light beam and is related to the linear electro-optic coefficient r_{14}. The values for $g(E)$ in the 380–450 nm wavelength range have been obtained experimentally and are reported in the Ref. 10.

For the case of crystals with a diamond structure, all the elements of the linear electro-optic tensor are zero and so the term $g(E) = 0$ for all wavelengths. Then, we do not expect any anisotropy arising from the bulk of these crystals. Therefore, if a structural transition from zincblende to diamond in metastable $(\mathrm{GaAs})_{1-x}\,(\mathrm{Si}_2)_x$ alloys exists, we must observe experimentally that the anisotropy signal disappears for a certain value of x.

3. EXPERIMENTAL SYSTEM

The experimental system used for the detection of the zincblende-diamond structural transition by RDS is shown in Fig. 1. The technique consists in focus linearly polarized light on the sample we want to analyze. The sample is rotating at a fixed frequency and then the light is polarized parallel to different symmetry directions of the sample. The light reflected from the sample is detected by a photodiode that converts the luminous signal in an electronic signal and send it to a lock-in amplifier. The lock-in amplifier receives also a reference signal from the rotor where the sample is located. Thus, the lock-in amplifier eliminates all the signals vibrating at frequencies different from the sample rotation frequency. If we select in the lock-in amplifier the $2f$ mode, it takes

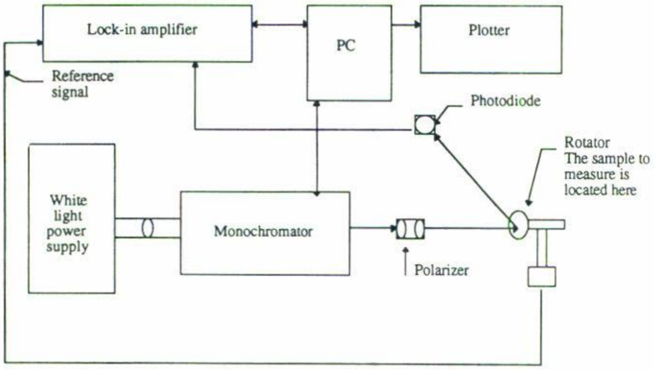

FIGURE 1. Experimental system used for the detection of zincblende to diamond structural transitions.

a measurement every 90° and therefore if an anisotropy exists in the sample we can obtain a signal that is the difference in reflectivity between two perpendicular symmetry directions of the crystal. The wavelength resolution of the system was 0.1 nm. More details about RDS technique are given in the Ref. 13.

For this experiment we used a GaAs crystal, (100) oriented, with a doping concentration of about $10^{17}/\mathrm{cm}^3$, as the $x = 0$ sample. Metastable $(\mathrm{GaAs})_{1-x}\,(\mathrm{Si}_2)_x$ alloys with silicon concentrations of the order of 8.5% to 37%, were measured to detect the structural transition. These samples were epitaxial metastable layers grown on As-stabilized (100) GaAs substrates by a sputter-deposition-evaporation hybrid technique [14]. The surface of all the samples had a mirror like appearance, except for the sample with $x = 0.20$ that presented some surface imperfections.

The samples were cleaned only with methanol and rinse with a nitrogen flux. They were fixed to the rotor with silicon paste and aligned previously to the experiment using a He-Ne laser and a beam position detector.

As has been previously reported [13], the electric field responsible for the observed electro-optic effect arises because of the presence of surface states at the oxidized GaAs surface, that pin the Fermi level originating a surface band bending [12]. The presence of this electric field causes that semiconductors with zincblende lattices (like GaAs) become uniaxial and therefore that a bulk anisotropy appears. On the other hand, semiconductors with a diamond structure (like Si) do not change their cubic symmetry due to the presence of an electric field and then we do not expect a bulk anisotropy in the RDS spectra of these semiconductors.

4. RESULTS AND DISCUSSION

We measured the anisotropy spectra of a GaAs crystal and of several $(\mathrm{GaAs})_{1-x}\,(\mathrm{Si}_2)_x$ samples with the following concentrations of x: 0.085, 0.10, 0.20, 0.23, 0.30, 0.37. In these measurements we generally obtain a graphic of the normalized reflectivity change $(\Delta R/R)$ as a function of the photon energy of the incident light. The measured spectra are shown in Fig. 2.

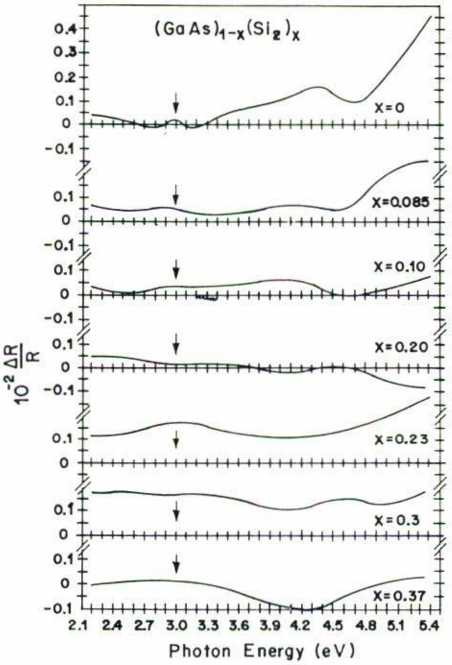

FIGURE 2. Anisotropy spectra obtained for several metastable $(\mathrm{GaAs})_{1-x}(\mathrm{Si}_2)_x$ alloys, with different silicon concentrations given by x. The arrows shown in the figure indicate the position of the transition energy E_1 for GaAs.

As we show in previous publications [10, 15], the anisotropy spectra are formed by two components: one arising from the bulk of the semiconductor and another one from the surface of the crystal. The bulk effects are the responsible for the oscillation observed around the transition energy E_1 at 3 eV. Surface effects affect the spectra only by a d.c. shift or by lightly deforming them [15], specially for high photon energies.

If we observe the spectra in Fig. 2, we see that the oscillation around the transition energy at 3 eV is very well defined for GaAs. This oscillation becomes smoother as x increases, that is, as more gallium and arsenic sites are occupied by silicon atoms. For x about 0.37, the oscillation disappears.

When concentrations of the atoms of two semiconductors with different original lattices exist together with the same order of magnitud, we expect a transition from one lattice to the other at a certain value of the x concentration of one atom. In this case, we start from a GaAs lattice that posseses a zincblende structure. As more and more atoms of gallium and arsenic are substituted by silicon atoms, the crystal losses the memory of its original lattice (zincblende) and behaves as a crystal with the silicon structure (diamond).

According to the electro-optic effect theory, the characteristic oscillation of the anisotropy spectra for gallium arsenide, should not be present in the anisotropy spectra of silicon, because there is not an anisotropy arising from the bulk of these semiconductors due to their high symmetry. Therefore, if a structure is observed in the silicon spectra,

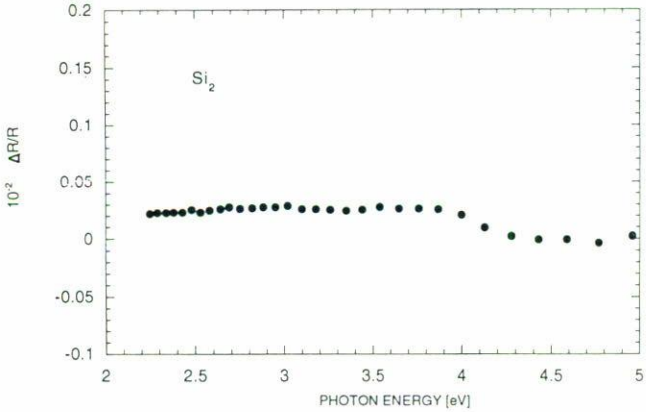

FIGURE 3. Anisotropy spectrum of a silicon epitaxial layer.

it should come from surface effects. To show this, we measured the anisotropy spectrum of a silicon epitaxial layer grown in the laboratories of the Centro de Investigación y Estudios Avanzados in Mexico, by a liquid-phase epitaxy process. Silicon epitaxial layer was 8×10^{17} cm^{-3} and (100) oriented. The resultant spectrum is shown in Fig. 3. The sample was cleaned with methanol and rinse with an air flux.

We observe that the characteristic oscillation that appears in GaAs around 3 eV is not present. However, some structure is still present for higher energies which we consider that is related to surface effects, such as micro-roughness. The similarities between the last spectrum of Fig. 2 and the spectrum of Fig. 3 are notable.

It is important to note that the spectrum shown in Fig. 3 differs from the RDS spectrum reported by other authors [9] where RDS spectrum for (100) Si shows no structure. In fact we do not expect anisotropies arising from the bulk of this semiconductor as the linear electro-optic effect is not present. This is the reason for the flatness of the spectrum for (100) Si in the 2.1 to 3.5 eV energy range. However, as has been pointed out previously [2, 3, 15] surface anisotropies can be expected, arising from the truncation of lattice because of the presence of a surface, as well as from micro-roughness. These surface anisotropies are more evident around the E_0' and E_2 transitions [2, 3, 15] and in addition to deform the spectra for high energies, may induce a vertical shift of the spectra [15].

To better observe the change in the structure of the spectra as the silicon concentration increases, we obtained the first derivative of the spectra shown in Fig. 2, as a function of the photon energy. The resultant spectra are shown in Fig. 4. The valence-conduction bands transitions E_1, E_0', and E_2 are also indicated in this figure for the case of GaAs. We can observe a very rich structure around the transition energies for GaAs, which starts to smooth as the silicon concentration is of the order of 8.5%, becoming finally in just a smooth undulation when the silicon concentration rises the 37%. In fact, the two characteristic maxima observed around the E_1 transition for GaAs, become in just one maximum as soon as $x = 0.085$ and dissappear for $x = 0.37$. In a previous paper, other authors have explained this change in structure on the basis of surface effects [9]. However, we consider that if a change in the structure of a crystal occurs, this change

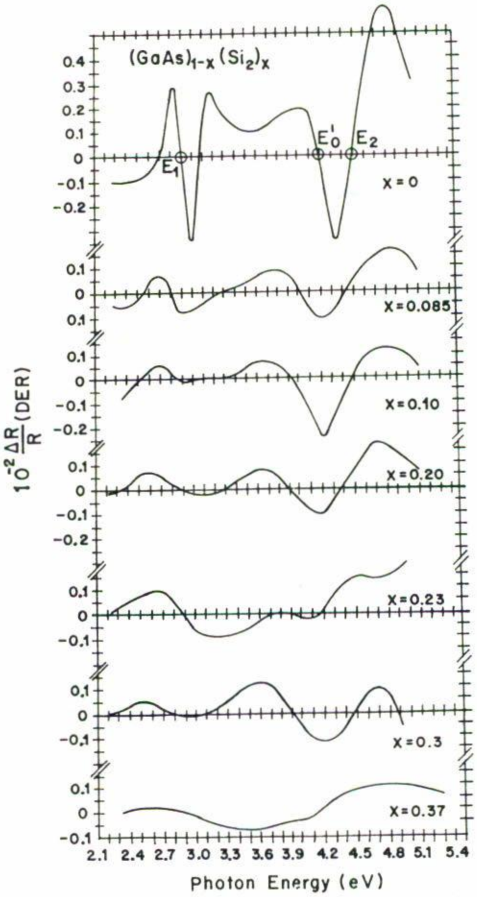

FIGURE 4. First derivative of the anisotropy spectra shown in Fig. 2, with respect to the photon energy of the incident light.

must affect principally the bulk of the crystal and therefore the explanation must be given on the basis of bulk effects, such as the electro-optic effect. Furthermore, in Ref. 9 the authors reported the zincblende-diamond transition around $x = 0.37$, but they did not measured the anisotropy spectrum of a sample with this concentration. They obtained this value for x, from X-ray diffraction measurements. Therefore, the RDS spectrum of $(\mathrm{GaAs})_{1-x}\,(\mathrm{Si}_2)_x$ for a silicon concentration of 37% is being reported in this paper for the first.

5. CONCLUSIONS

It has been shown that Reflectance Difference Spectroscopy is a powerful technique to detect structural changes from anisotropic lattices (zincblende in presence of an electric field) to isotropic lattices (diamond). The experiments carried out show that in metastable $(\mathrm{GaAs})_{1-x}\,(\mathrm{Si}_2)_x$ alloys, the structural transition occurs for a silicon concentration of about 37%. This result is in agreement with the results obtained for other authors using X-ray diffraction patterns [7, 9]. Samples with higher silicon concentrations where not available and therefore we can not measured metastable alloys with higher values of x.

The advantages of using the RDS technique are:

a) RDS is a non-destructive technique,
b) the installation and measurements are easy,
c) the experiments are carried out under normal pressure and temperature conditions,
d) the results are seen directly from the measured spectra.

The zincblende to diamond structural transition has been explained on the basis of the linear electro-optic effect, which is present for zincblende crystals, but not for diamond crystals. The RDS spectrum for metastable $(\mathrm{GaAs})_{1-x}(\mathrm{Si}_2)_x$ alloys with $x = 0.37$ is reported for the first time in this paper.

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