Superficies y Vacío 1, 53-58(1989)

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REFLECTANCE-DIFFERENCE SPECTROSCOPY: AN OPTICAL PROBE FOR THE STUDY OF SURFACE PROCESSES IN CUBIC SEMICONDUCTORS

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We report measurements of optical anisotropies in the reflectivity spectrum of, both, (001) and (110) surfaces of GaAs (2.4-5.5 eV photon energy range). We disscus the several components that comprise the anisotropy spectra. For GaAs (110), we isolate the quadratic electro-optic component of the anisotropy spectrum. For GaAs (001), we report the spectrum component associated to oxigen bond to the GaAs surafce. Furthermore, we describe two spectrometers for the measurement of optical anisotropies in the reflectivity spectra of cubic semiconductors.

INTRODUCTION

Reflectance-Difference Spectroscopy (RDS) is a promising tool for the study of surface processes in cubic semiconductors [1-11]. This spectroscopy has been shown to be useful in the study of bromine adsorbates in germanium [3], and in the *in situ* characterization of the epitaxial growth of GaAs and (GaAl)As by MBE [10] and GaAs by MO-CVD [10]. For MBE, RDS provides complementary information to that offered by the electronic characterization techniques available in Ultra High Vacuum systems [10]. As such techniques are no available for chemical vapor deposition reactors, due to their high working pressure, RDS becomes particularly important for the study of CVD epitaxial growth processes [11]. It is noted that RDS, as an optical technique, is not necesarily ruled out in high pressure enviroments.

The working principle of RDS is based on the fact that, as the bulk optical properties of cubic semiconductors are nominally isotropic, any observed anisotropy in the reflectance spectrum should be due to the breakdown of the cubic symmetry associated to the semiconductor surface [2-4]. Then, by measuring the difference in reflectance for two mutually perpendicular light polarizations, the bulk contribution to the sample reflectivity should be filtered out, remaining only the surface contribution.

It is now clear, however, that the anisotropy spectra of, both, (001) and (110) surfaces of GaAs are formed by the superposition of several components with various physical origins [6-9]. Surface as well as bulk components can appear. Surface components are associated to the first surface monolayers, while bulk components originate in a region hudreds of monolayers wide, below the semiconductor surface. It is then essential to have a clear picture of all the components present in the anisotropy spectrum in order for RDS to be useful in the study of surface processes.

It has been reported that bulk anisotropies can appear because of, both, spatial dispersion effects [6] and electro-optic effects [7-9]. Regarding the electro-optic mechanisms, bulk anisotropies arise because of the breakdown of the cubic zincblende symmerty of GaAs by the surface electric field present at the oxidized GaAs surface [7-9]. Both, linear [8] and quadratic [9] electro-optic effects can appear. On the other hand, among the sources for surface anisotropies we mention surface local field effects [2-4] and adsorbed molecules [3].

In this paper we report measurements of optical anisotropies in the reflectance spectra of GaAs, both, (001) and (110) and discuss the several components that comprise

them. Specifically, we report the quadratic electro-optic component of the anisotropy spectrum of GaAs (110) in the energy range including the E_1, $E_1+\Delta_1$, E'_0 and E_2 optical transitions as well as the surface component due to oxigen bonded to the (001) surface of GaAs. Furthermore, we describe two spectrometers for the measurment of optical reflectance anisotropies. In one of the spectrometers the sample rotates at a fixed frequency while in the other the sample is kept fixed modulating instead the polarization of the incident light. Although the two spectrometers give essentially the same information, the photoelastic modulator instrument is the only choice in applications such as the study of epitaxial growth processes, where the sample has to be static.

EXPERIMENTAL

Two different spectrometers were used for the measurement of the anisotropy spectra. In the first instrument, monochromatic, linear polarized light, incides on the sample which is kept rotating at a frequency of about 25 Hz (figure 1). Any anisotropy in the optical properties of the sample surface would result in a modulation of the reflected light intensity at a frequency twice as large as the sample rotating frequency. After reflection, the light is focused on a UV enhanced silicon photodiode/amplifier combination (United Detector Technology, model UDT 555 UV). Standard lock-in techniques are used to isolate the modulated component of the sample reflectivity. Spherical mirrors are used to focus the light in order to make the system achromatic. For the purpose of alignement, the sample is fixed on a kinematic mount with three adjustable screws. More details are given elsewhere [7,8].

In the second spectrometer (figure 2) the sample is kept fixed, modulating instead the polarization of the incident light by means of a photoelastic modulator (Hinds International, model PM-80). The heart of the modulator is a fused silica optical element which becomes birrefringent by the application of a time-dependent stress along the modulator axis. Linearly-polarized light entering the modulator with the polarization vector making an angle other than zero with its optical axis, will emerge in general elliptically polarized, as the retardation of the light polarization components paralell and perpendicular to the modulator axis are in general different.

In the experiment, monochromatic light is first passed through a linear polarizer (quartz rochon prism) and then through the photoelastic modulator. The optical axis of the the polarizer is oriented so that the light polarization vector incides on the modulator making a 45 degree angle with its optical axis. Furthermore, the relative peak retardation length between the two light polarization components is chosen equal to $\lambda/2$, with the result that the polarization of the light exiting the modulator oscillates between two linear states with polarization vectors 90 deegres apart. In between the two extreme states elliptic polarization is obtained (circular polarization is obtained for the intermediate retardation length of $\lambda/4$). The orientation of the sample is chosen so that its optical axis coincides with the two extreme polarization states, in such a way that a maximun anisotropy signal is obtained.

As pointed out before, both spectrometers described in this section give essentially the same information. It is however noted that, althought the photoelastic modulator spectrometer has the advantage of keeping the sample static, it is prone to the appareance of artifacts. This can be understood if we consider that, after the light exits the photoelastic modulator, its polarization is modulated, so that any non-normal incidence on the subsequent optical surfaces (sample, depolarizer, focusing lens and photodetector, see figure 2) would result in a parasitic modulation of the light reaching the active region of the silicon photodetector. The parasitic component due to this modulation will add up to the anisotropy spectrum. The parasitic component can be, however, eliminated by taking a second spectrum with the sample rotated 45 degrees with respect to the orientation that maximizes the anisotropy signal; this second spectrum should have no intrinsic component, so that by substracting it to the first spectrum, the parasitic component should be eliminated.

The samples used in the measurements were Czochralski grown, (001) and (110) oriented GaAs crystals doped either with Cr (semi-insulating) or with silicon donors at levels in the 1-2 x $10^{18}/cm^3$ range. Prior to the experiments, the crystals were given a chemomechanical polish with 1% Br in methanol, rinsed in methanol and dryed with a N_2 flow.

EXPERIMENTAL RESULTS AND DISSCUSION

We will first discuss the results regarding the GaAs (110) samples. The two upper curves of figure 3 show the reflectance anisotropy for two GaAs crystals. Uppermost curve corresponds to a sample doped with Si donors at a level of 1.2 x $10^{18}/ cm^3$, while middle curve corresponds to a Cr doped semi-insulating sample. As it can be seen, there is a difference between both curves

which is larger in the region around the E_1 and $E_1 + \Delta_1$ transitions (2.4 - 3.5 eV). Lowermost curve in figure 3 shows the difference spectrum obtained by substracting the middle curve to the upper curve of the same figure.

The difference spectrum of figure 3 is explained on the basis of a quadratic electro-optic effect. Indeed, the Si doped sample has a surface electric field (due to Fermi level pinning at surface states) of the order of 10^5 V/cm. This field is large enough to produce reflectivity changes $\Delta R/R$ of the order of 10^{-3} [12] which are anisotropic for normal incidence on the (110) surface [13]. Thus, an electro-optic component should be present in the reflectance anisotropy spectrum of the Si doped sample. Furthermore, this electro-optic component should be quadratic in the electric field as it is known that, in a longitudinal geometry, no linear electro-optic effects can appear for normal incidence on a (110) zincblende surface [13].

For the Cr doped GaAs sample, on the other hand, the surface electric field is negligible, so that the middle spectrum of figure 3 should be free of electro-optic components. Thus, the difference spectrum of figure 3 should correspond entirely to the quadratic electro-optic component.

Previously [9], a similar conclusion was reached by comparing, in the energy region around the E_1 and $E_1 + \Delta_1$ transitions, the electro-optic component of the anisotropy spectrum of a sample of GaAs (110) with the quadratic electroreflectance spectrum of the same sample. Both spectra were shown to agree closely. The lower curve of figure 3 shows the electro-optic component of the anisotropy spectrum of GaAs (001) in an extended energy region comprising the E_1, $E_1 + \Delta_1$, E'_0 and E_2 transitions. As expected from the bulk electro-optic origin of this component, its optical structure appears correlated to the critical point transition energies (shown by arrows in figure 3) of the band structure of GaAs.

Let us now consider the reflectance anisotropy spectrum of GaAs (001) Previously [8], it was shown that, given a strong enough surface electric field, an electro-optic component appears in such anisotropy spectrum. However, in contrast to what happens for GaAs (110), the electro-optic component of GaAs (001) instead of quadratic, is linear in the electric field [8]. In what follows we will shown that besides the electro-optic component of the GaAs (001) anisotropy spectrum, there is a second component which is associated to oxigens bond to the semiconductor surface. In contrast to the electro-optic component which constitutes a bulk effect, this second component originates in the first monolayers of the semiconductor surface.

The upper curve of figure 4 corresponds to the anisotropy spectrum of a (001) oriented GaAs crystal which was annealed in vacuum (10^{-6} torr) for 10 minutes at a temperature of 600 °C. After the measurement, the sample was annealed in air at 350 °C for a few minutes and the anisotropy spectrum was again measured. Middle curve in figure 4 shows the obtained result. It is noted that we can go back and forth between the upper and middle curves by sucesive annealings in vacuum and air so that the process is reversible.

The lower curve of figure 4 was obtained by substracting the middle spectrum to the upper spectrum of the same figure and thus corresponds to the anisotropy spectrum of oxigen bond to the GaAs surface. The fact that annealings in air and vacuum produces changes which are reversible suggests that the difference spectrum of figure 4 is associated to the first surface monolayers.

The existence of an anisotropy associated to oxigen bond to the (001) GaAs surface could be understood if we assume that this surface is terminated preferentially in either Ga or As atoms. Surface dangling bonds would have then a preferential orientation as will do oxigens bond to surface atoms.

The results described in the above section indicate that the optical anisotropy spectra of, both, (001) and (110) GaAs surfaces are rather complex and are formed by the superposition of several components. Such components could originate in surface effects as well as in bulk effects. Considering figure 3, we conclude that the GaAs (110) anisotropy spectrum has at least two components. First, a quadratic electro-optic component (lower spectrum) which is essentially a bulk effect and second, an impurity independent component (middle spectrum) whose origin is not established at present but that may be associated to the breakdown of the GaAs cubic symmetry due to the presence of the semiconductor surface [2-4]. As additional possible components present in the middle spectrum of figure 3 we can not discard components due to spatial dispersion effects [6] as well as effects associated to atoms adsorbed on the GaAs surface.

Regarding the GaAs (001) anisotropy spectra we can definitely establish that at least three components may appear. First, a linear electro-optic component which is a bulk effect and that, as shown before [7,8]

is most important in the region around the E_1 and $E_1 + \Delta_1$ transition energies second, a component associated to oxigen bond to the GaAs surface (middle curve of figure 4) and third, a component whose origin is not clear at present but that, as in the case of GaAs (110), may be associated to the termination of the atomic lattice at the semiconductor surface.

CONCLUSIONS

We conclude that the optical anisotropy spectra of, both, (001) and (110) surfaces of GaAs show several components with different physical origins. Both, bulk and surface phenomena can contribute to such spectra. Regarding the (110) GaAs surface, we determined the bulk-related quadratic electro-optic component, in the 2.5-5.5 eV photon energy range which comprise the E_1, $E_1 + \Delta_1$, E'_0 and E_2 transitions. For the (001) GaAs surface we isolated the surface-related component associated to oxigen bond to the semicondctor surface. These results are important for the application of RDS to the analysis of surface phenomena in cubic semiconductors.

Furthermore, we have described two spectrometers for the measurement of optical anisotropy spectra of cubic semiconductors. In the first spectrometer, the sample is rotaing at a fixed frequency, while in the second one the sample is kept staic modulating instead the polarization of the incident light.

AKCNOWLEDGMENTS

The authors would like to thank valuable disscusions with D.E. Aspnes as well as to acknowledge his advise in the design of the photoelastic modulator spectrometer. Disscusions with R.G. Barrera and L.W. Mochan are also highly appreciated. This work was parttially supported by DGICSA-SEP, CONACyT (DADC, DAAI and DAFRHU), PRDCyT-OEA, and FAI-UASLP.

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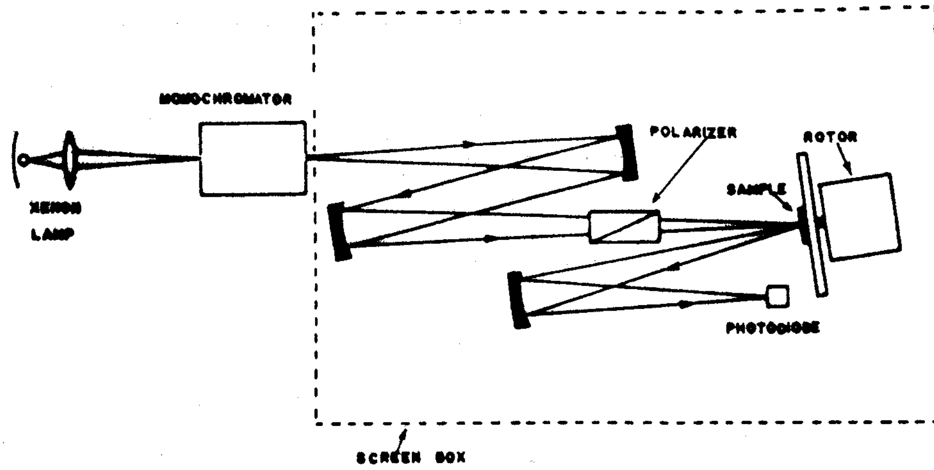

Figure 1. Rotating sample spectrometer for the measurement of anisotropies in the reflectivity spectra of cibic semiconductors.

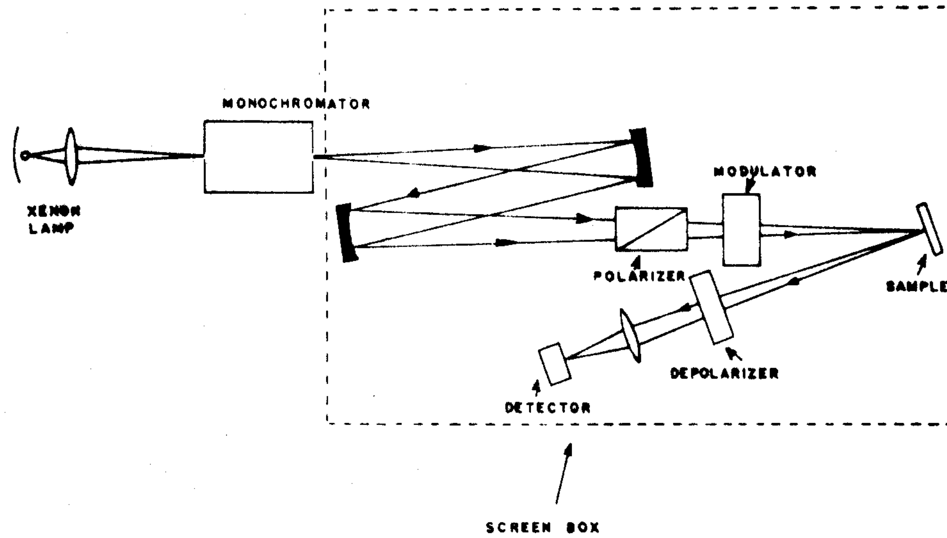

Figure 2. Photelastic modulator spectrometer for the measurement of anisotropies in the reflectivity spectra of cubic semiconductors.

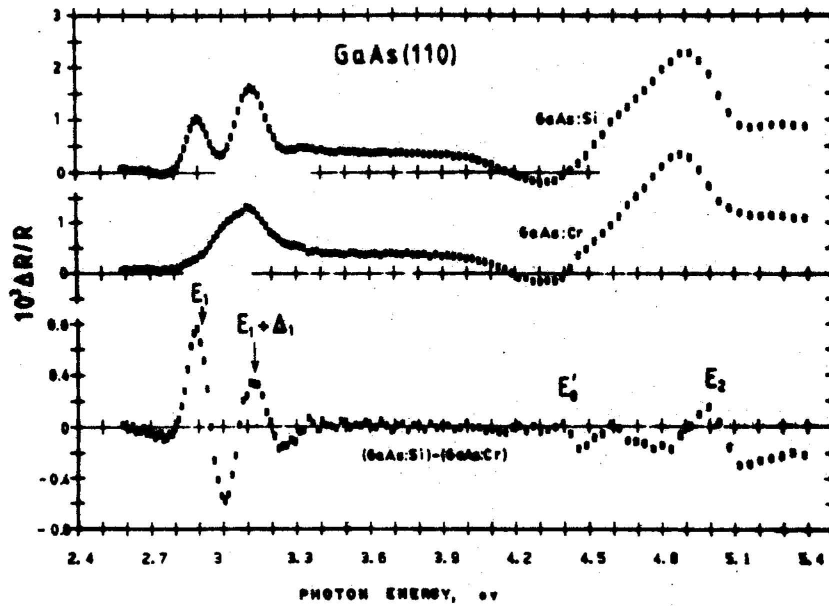

Figure 3. Reflectance-Difference spectra for the (110) surface of GaAs. Upper curve: Si doped GaAs at a level of $1.2 \times 10^{18}/cm^{3}$; middle curve: Cr doped GaAs; lower curve: difference spectrum obtained by substracting the middle spectrum to the upper spectrum.

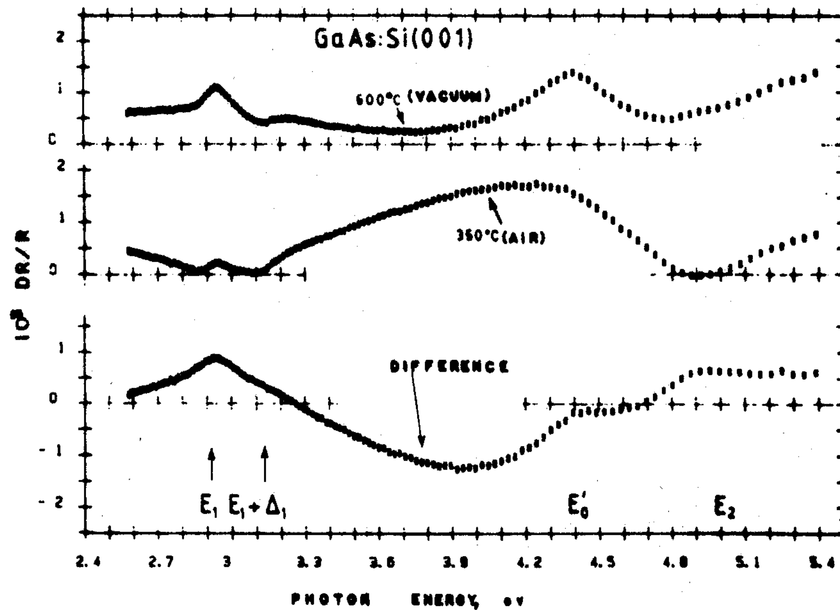

Figure 4. Reflectance-Difference spectra for the (001) surface of GaAs. Upper curve: GaAs annealed in vacuum at 600°C; middle curve: GaAs annealed in air at 350°; lower curve: difference spectrum obtained by substracting the middle spectrum to the lower spectrum.