

Optical and structural characterization of the heterostructure CdTe/GaAs grown by RF sputtering

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We present the results of the characterization of CdTe thin films grown by radio frequency sputtering employing GaAs substrates subject to different chemical cleaning procedures. The objective of this work is to study the effect of GaAs fresh oxides on the properties of CdTe films. The three different chemical procedures were: (1) $\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} +$ deionized water rinse, (2) $\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} +$ deionized water rinse and (3) $\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} + \text{HF} +$ deionized water rinse. The samples were stoichiometric within 2% as obtained from energy dispersive X-ray analysis. X-ray measurements showed that a preferential growth was obtained and it was in the (111) direction. Photoluminescence measurements showed that the signal coming from the GaAs substrate had an important contribution, this is explained in terms of the presence of electric fields originated at the interface CdTe/GaAs. The presence of internal electric fields was confirmed by photoreflectance measurements. Raman spectroscopy measurements showed a broadening for the TO and LO optical phonon modes, probably due to the presence of micro crystals. However, the full width at half maximum is low for the usual values found for CdTe films grown by RF sputtering. From photoluminescence measurements we can say that the procedure 1 yields material with the best characteristics.

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I. INTRODUCTION

CdTe is a very attractive material for applications such as γ -ray and X-ray detectors, photovoltaic material and substrate for infrared detectors based on HgCdTe.[1,2,3,4] However the full exploitation of its potential has been hindered by the difficulties found to produce high quality single crystals. Even so, there are reports dealing with devices produced employing polycrystalline CdTe films.[5] One approach to produce good quality, high area CdTe material is the growth of CdTe on high quality substrates with similar lattice parameters.[6,7,8] Because of the availability to use high quality GaAs substrates at reasonable cost, the production of CdTe/GaAs heterostructures has deserved a good deal of work. In order to grow the CdTe/GaAs heterostructures a variety of deposition techniques has been employed. Here we present the results of a structural and optical characterization of CdTe films grown by r.f. sputtering on GaAs(100). The CdTe films were grown on GaAs substrates subject to three different chemical processes in order to obtain fresh GaAs-related oxides prior to deposition: (1) $\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} +$ deionized water rinse, (2) $\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} +$ deionized water rinse and (3) $\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} + \text{HF} +$ deionized water rinse. It has been established that acidic etchings on GaAs renders arsenic-related oxides, while alkaline etchings produces gallium-related oxides.[9] We

expect that procedure 3 gives a mixture of Ga and As related oxides, being the content of As oxides more important. The CdTe/GaAs heterostructures were studied through experiments of photoluminescence at 14 K, room temperature photoreflectance and Raman spectroscopies, X-ray diffraction and scanning electron microscopy. The quality of the CdTe thin films depends on the substrate preparation process and there is a clear trend indicating that the best film is that grown when the substrate is prepared under process 1.

II. EXPERIMENTAL DETAILS

A set of four CdTe films were deposited on semi-insulating GaAs (100) substrates subject to different cleaning processes. In order to have a control sample one of the GaAs substrate was cleaned employing a standard procedure without using any etching agent. The other samples were subject to three different cleaning processes, which produced fresh surface oxides. The details of the cleaning process are presented in Table I, briefly they consist of: (1) $\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} +$ deionized water rinse, producing As rich oxides (2) $\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} +$ deionized water rinse, producing Ga rich oxides and (3) $\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} + \text{HF} +$ deionized water rinse, producing As rich oxides. After the cleaning process the GaAs substrates were transferred in air to the sputtering chamber. The samples are labeled

TABLE I: Chemical etching treatments employed in the preparation of the GaAs substrates

| Chemical etching procedure Sample 1A | t(s) | Chemical etching procedure Sample 2A | t(s) | Chemical etching procedure Sample 3A | t(s) |
|--|------|--|------|--|------|
| H ₂ SO ₄ | 90 | | | | |
| H ₂ SO ₄ : H ₂ O ₂ : H ₂ O 3 : 1 : 1 | 30 | NH ₄ OH : H ₂ O ₂ : H ₂ O 2 : 1 : 300 | 180 | NH ₄ OH : H ₂ O ₂ : H ₂ O 2 : 1 : 300 | 180 |
| | | | | HF | 600 |
| Deionized H ₂ O rinse | 600 | deionized H ₂ O rinse | 600 | deionized H ₂ O rinse | 600 |

according to the cleaning procedure. The films were grown from a target made of 5N purity CdTe-powder pressed employing a pressure of 20×10^8 Pa. The base pressure in the sputtering system was 10^{-6} Torr, an Ar pressure of 5×10^{-3} Torr and a radio-frequency power of 60 Watts were employed during the growth process. The deposition time was in all cases 10 min, with a substrate temperature of 180 °C. This temperature was chosen because corresponds to the maximum temperature achievable in our sputtering system. X-ray analysis were carried out in a Siemens D5000 diffractometer which uses the Cu-K α line. Film thicknesses and composition were obtained, respectively, from the images and from the analysis of the electron dispersed X-rays in a scanning electron microscope. Room temperature photoreflectance measurements were carried out employing a standard setup in which the 632.8 nm line from a He-Ne laser was used as modulator. Photoluminescence measurements were done at 14 K employing a He closed-cycle refrigerator; the 632.8 nm and 568 nm lines from He-Ne and Kr lasers were employed as excitation sources. A 0.5 m focal length single monochromator equipped with a GaAs photomultiplier was employed to analyze the photoluminescence signal. Room temperature Raman spectroscopy experiments were carried out in a Labram micro Raman system in which the sample is excited with a 20 mW He-Ne laser.

III. RESULTS AND DISCUSSION

The thickness of the four samples was around 0.9 μm as it was obtained from transversal scanning micrographs while electron dispersive X-ray analysis indicated that the composition was near of stoichiometry, there was a slight deficiency of around 2 % of Te. Figure 1 presents X-ray diffractograms of the studied samples, from them it is inferred that the CdTe thin films grew preferentially parallel to the (111) planes. The different intensity of the GaAs related peaks is attributed to differences in the parallelism between the substrate and sample holder during the measurement. Figures 2 and 3 present the results of 14 K photoluminescence obtained with two different laser lines, as indicated in each case. We can observe, as expected because of the different chemical treatment, changes in the GaAs and CdTe photoluminescence signals. Because of the penetration depth of the 632.8 nm He-Ne

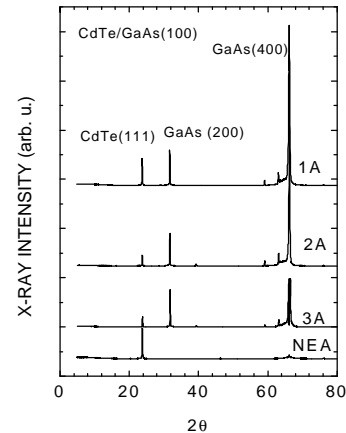


FIG. 1. X ray diffractograms of the studied samples, NEA stands for the not etched sample.

wavelength in CdTe (~200 nm)[10] we expected that most of the PL signal came from the CdTe thin film. However it is clear from figure 2 that the most important signal arises from the GaAs substrate. This could be explained taking into account the presence of an interfacial built-in electric field. When the hole-electron pairs are produced, a drift towards the GaAs/CdTe interface is experienced, and as consequence, the PL is excited in the GaAs by the carriers originally produced in the CdTe film. The presence of a strong GaAs signal could be an indirect evidence of a good crystalline quality of the CdTe film. Because even when the CdTe PL signal is low, carriers are not trapped and are able to reach the GaAs substrate. The features associated with GaAs are ascribed to carbon impurities (~1.49 eV) and excitonic related transitions (~1.514 eV).[11] It is noteworthy that for sample 1A, Fig. 2, the PL signal coming from the GaAs excitonic features increases with relation to the carbon feature. This could be interpreted as an increase in the purity of the GaAs region affected by the chemical etching. As an indication of the good quality of the CdTe films we can mention that the CdTe PL signal (~1.59 eV)[12] is present for this sample, although it is of lower intensity. In order to gain further insight on the CdTe characteristics through PL spectroscopy we perform experiments with the 568 nm line of a Kr laser. The penetration depth at this wavelength for

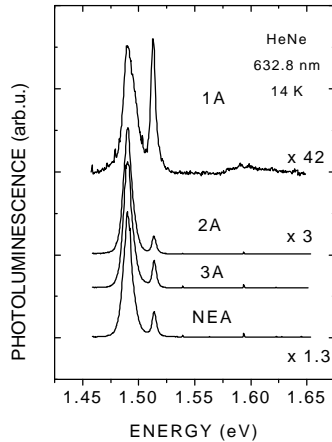


FIG. 2. Room temperature photoluminescence spectra of the studied samples obtained with the 632.8 nm wavelength of the He-Ne laser, NEA stands for the not etched sample.

CdTe is around 100 nm and as expected, see figure 3, the intensity of the CdTe PL signal is increased for the whole set of samples. Here we also observed the presence of a PL signal coming from GaAs, but except for sample 3A, the excitonic related feature is greater than the one related to carbon impurities. Because of the stronger absorption in CdTe of light of 568 nm wavelength, a lower amount of photogenerated carriers could reach the bulk GaAs. Therefore, the recombination near the CdTe/GaAs interface would be more important and it is reflected in the PL signal. The increase in the GaAs excitonic feature could be due to a reduction of the carbon impurities in GaAs near of the CdTe/GaAs interface due to the chemical etching. Figure 3 shows that now the CdTe signal appears for the whole set of samples but some differences can be noted. If we compare the ratio between the PL intensities of the CdTe and the carbon related signal of GaAs, we could say that heterostructure 3A presents lower-quality characteristics than that obtained with no etching of the substrate. The combination of CdTe PL intensity and the low interfacial carbon content of GaAs, as inferred from its PL intensity, may allow us to say that chemical treatments 1A and 2A produced films with good characteristics, and that treatment 1A produced the best-quality CdTe film.

Figure 4 presents room temperature photoreflectance spectra of the whole set of samples. It is clear the presence of signals coming from GaAs and CdTe around 1.41 eV and 1.56 eV, respectively. These values are obtained from fittings to the third derivative line form based on the electroreflectance theory of Aspnes [13]. We employed two signals, one for GaAs and other for CdTe, the fittings are presented as open circles. Even when fittings could be improved, they provide a close idea of the band gap values. The presence of a GaAs signal could be hard to explain if we considered only the penetration depth of 632.8 nm light

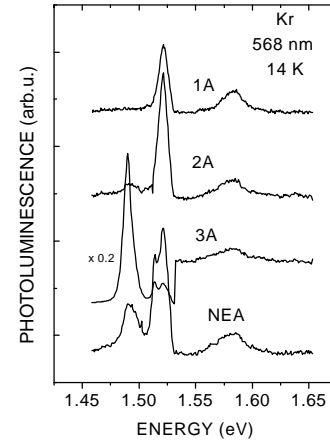


FIG. 3. Room temperature photoluminescence spectra of the studied samples, obtained with the 568 nm wavelength of the Kr laser, NEA stands for the not etched sample. Note the scale factor for spectrum 3A in the GaAs signal region.

which is around 200 nm as mentioned before, but again the presence of a GaAs signal in the photoreflectance spectrum is a qualitative indication that the CdTe film has good quality because the photogenerated carriers can reach the GaAs substrate. It is clear from figure 4 that the region between the GaAs and CdTe signals could not be fitted, there is an additional structure, see spectrum 1A. This structure is due to the presence of a built-in electric field at the CdTe/GaAs interface.[14] This is in agreement with the explanation about the origin the GaAs PL signal and also explains the presence of the GaAs photoreflectance signal. The same arguments mentioned for the origin of the GaAs PL signal apply in photoreflectance: the presence of an interfacial electric field which drives carriers toward the GaAs increasing the diffusion length of the photogenerated carriers. Figure 5 presents the Raman spectra for the whole set, we expected the presence of both the TO and LO CdTe optical phonon modes, because from the X-ray results a preferential growth in the [111] direction was established.[15] The LO mode is clearly present while the TO mode could be identified at the low energy side of the Raman spectra. It is possible that the reason because the modes merged is the broadening due to micro crystals, however, this should be reflected in both modes. Something worth to mention is the absence of peaks due to telluride and the rather narrow full width at half maximum of the LO CdTe phonon. The presence of an overtone of the LO phonon frequency is observed, which is an indication of the good structural quality of the materials. Note that from the structural point of view, the samples have slight differences. Thus, it may be stated that the different preparation procedures yield CdTe films with similar structural characteristics that affect the radiative recombination characteristics, as shown by the PL measurements.

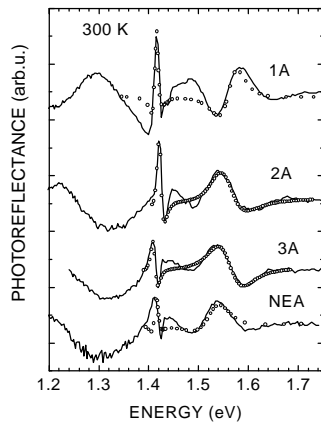


FIG 4. Room temperature photoreflectance spectra of the studied samples, NEA stands for the not etched sample. Open symbols correspond to the theoretical fitting to a third derivative model (see text).

IV. CONCLUSIONS.

CdTe/GaAs heterostructures having a preferential growth in the [111] direction were produced by r.f. sputtering. From photoluminescence results it was deduced that when a GaAs surface with a mixture of Ga and As related oxides is employed the optical properties of the films are degraded as compared with that obtained with a surface containing Ga or As related oxides. The presence of built-in electric fields is inferred from photoreflectance measurements, the origin of which is mainly associated with the band offset. The structural quality of the CdTe films is good as reflected in the absence of a Raman Te signal, frequently found in samples of poor quality.

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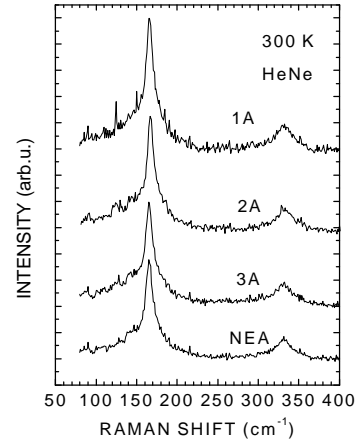


FIG 5. Room temperature Raman spectra of the set the samples studied. The small peak around 340 cm^{-1} corresponds to an overtone of the LO optical phonon mode, NEA stands for the not etched sample.

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