



ELSEVIER

Applied Surface Science 123/124 (1998) 261–265

applied  
surface science

# Optical properties of semimagnetic semiconductors studied by thermoreflectance spectroscopy

H. Ariza-Calderon <sup>a</sup>, L. Tirado-Mejia <sup>a</sup>, J.G. Mendoza-Alvarez <sup>b,\*</sup>,  
O. Alvarez-Fregoso <sup>b</sup>, O. Zelaya-Angel <sup>b</sup>, S.A. Lopez-Rivera <sup>c</sup>

<sup>a</sup> *Lab. de Optoelectronica, Univ. del Quindío, A.A. 460 Armenia, Quindío, Colombia*

<sup>b</sup> *Depto. de Fisica-CINVESTAV-IPN, Apdo. Postal 14-740, Mexico DF, Mexico*

<sup>c</sup> *Depto. de Fisica, Univ. de los Andes, Merida, Venezuela*

## Abstract

The effect of introducing the magnetic elements Ni and Co into a II–VI host lattice, and their influence on the fundamental band gap energy, have been studied by means of thermoreflectance (TR) spectroscopy, following the evolution of the  $E_0$  transition at the  $\Gamma$ -point of the Brillouin zone, in terms of the magnetic ion concentration, and/or the film crystallite size. Two systems have been studied: (1)  $\text{Cd}_{1-x}\text{Ni}_x\text{Te}$  thin films grown by r.f. sputtering onto Corning glass substrates with Ni concentrations in the range:  $0 < x < 0.15$ . These films showed a nanocrystalline structure with the grain size decreasing as the film Ni content increases. From the TR spectra it was found that the band gap shifts to higher energies as the nanocrystalline size decreases, giving us evidence of a quantum-size effect due to electron confinement; (2)  $\text{Cd}_{1-x}\text{Co}_x\text{Se}$  crystals grown by the vapor phase chemical transport technique at a temperature of  $950^\circ\text{C}$ , for two concentration values:  $x = 0.01$  and  $0.05$ . As compared to a pure CdSe sample, the crystal with a Co concentration of 1 at% shows a shift of the  $E_0$  transition of about 70 meV to lower energies. For both samples, there appear additional oscillations in the low energy part of the TR spectrum which we interpret as due to the levels introduced by the Co-3d orbitals. The shifts of the  $E_0$ -point are also discussed. © 1998 Elsevier Science B.V.

PACS: 78.20.Nv; 75.50.Pp; 78.66.Hf

Keywords: Thermoreflectance spectroscopy; Diluted semimagnetic semiconductors; Optical properties of II–VI semiconductors

## 1. Introduction

Dilute semimagnetic semiconductors (DMS) have been the subject of an intensive research during the last decade because of the new effects which arise from either the exchange interactions between magnetic moments on magnetic ions, or between mag-

netic moments and the spin of the charge carriers.

These DMS are formed basically from II–VI, IV–VI or III–V semiconductors in which a fraction of the cations has been substituted by a magnetic transition metal or a rare earth ion. The incomplete d-shell in transition metals, or the 4f-shell in rare earths, of the magnetic atoms gives rise to a variety of properties in which their localized magnetic moments play an important role.

Most of the research performed on the DMS materials has been focused to the Mn-based DMS, in

\* Corresponding author. Tel.: +52-5-7477000, ext. 4209; fax: +52-5-7477096; e-mail: jmendoza@fis.cinvestav.mx.

particular in the family of  $\text{II}_{1-x}\text{Mn}_x\text{VI}$  alloys [1]; these DMS are the example of a permanent magnetic moments system.

Ni-based DMS's are interesting materials because Ni in the CdTe lattice acts as a deep and genuine 3d acceptor atom in CdTe and its behavior can be contrasted to other transition metal impurities such as Cu or Mn [2]. Recently [3], we have reported on the structure and electrical properties of CdNiTe thin films in which the microcrystalline grain size is close related to the Ni concentration in the film influencing also the electronic transport mechanisms in the film.

The Co-based DMS's are isostructural with their nonmagnetic counterparts. In the case of  $\text{Co}^{2+}$  ions in CdS and CdSe, these crystallize in the wurzite structure, and the picture is that of a  $\text{Co}^{2+}$  ion surrounded by four anions forming a regular tetrahedron with a small distortion; and so, the crystal field potential will have two terms: one with a tetrahedral symmetry and a second and much smaller with trigonal symmetry. The tetrahedral crystal-field produce a split of the free-ion ground term,  $^4\text{F}$  into a  $^4\text{A}_2$  orbital singlet and two orbital triplets,  $^4\text{T}_2$  [4]. The trigonal perturbation from the wurzite structure has the effect to split the fourfold degenerate  $^4\text{A}_2$  into two Kramers doublets [5]. This last splitting is responsible for an anisotropy of the magnetic susceptibility [6].

In this paper we present results on the optical properties of two different DMS's systems studied by thermoreflectance spectroscopy (TR), a technique that has been successfully used in the past to study another DMS:  $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$  thin films [7]. We have measured the TR spectra at room temperature of  $\text{Cd}_{1-x}\text{Ni}_x\text{Te}$  thin films grown by radio frequency (r.f.) sputtering with different Ni concentrations; and  $\text{Cd}_{1-x}\text{Co}_x\text{Se}$  crystals grown by the vapor phase chemical transport technique at two Co concentrations of 1 and 5 at%. From the analysis of the TR lineshape we obtained evidence of a blue-shift of the fundamental band gap transition of the  $\text{Cd}_{1-x}\text{Ni}_x\text{Te}$  films which is consistent with an interpretation of quantum-size effects due to the nanocrystalline nature of the grains in the films. In the case of the  $\text{Cd}_{1-x}\text{Co}_x\text{Se}$  crystals, the TR spectra have given us evidence of additional transitions below the one corresponding to the band gap which we have interpreted as due to the additional levels introduced when the  $\text{Co}^{2+}$  ions substitute the  $\text{Cd}^{2+}$  cations in the CdSe lattice. We also discuss the observed red-shifts of the  $E_0$ -transition as a function of the Co concentration in the crystal.

## 2. Experimental

$\text{Cd}_{1-x}\text{Ni}_x\text{Te}$  thin films were grown by the r.f. sputtering technique, the Ni concentration being

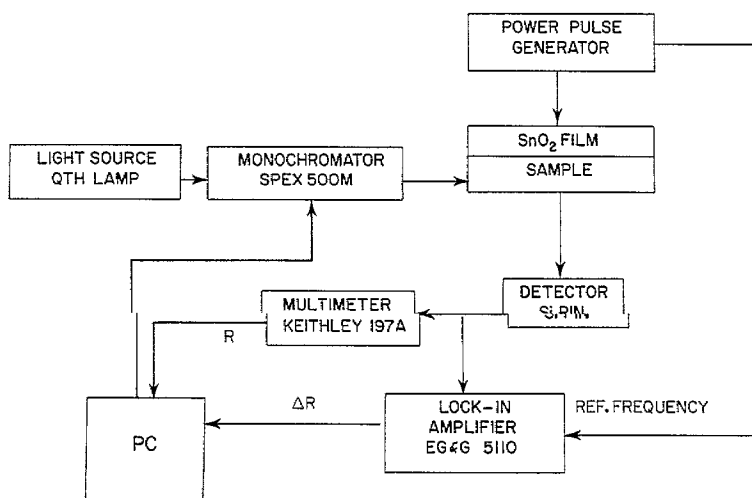


Fig. 1. Experimental setup for the thermoreflectance measurements. Sample is heating by placing it in contact with a glass slide covered with a  $\text{SnO}_2$  layer; an AC current is applied through the oxide layer.

changed by varying the Ni-plate size placed on top of the CdTe target. Typical growth parameters for the sputtering system have been described elsewhere [8]. X-ray diffraction patterns showed a zincblende parent structure with a preferential (111) orientation, and from a Scherrer's analysis of the main diffraction peak, it was found that the values for the grain size were: 35 nm ( $x = 0.05$ ); 30 nm ( $x = 0.10$ ); and 26 nm ( $x = 0.15$ ). Also, scanning electron microscopy studies done in these samples showed a well defined granular structure.

$\text{Cd}_{1-x}\text{Co}_x\text{Se}$  crystals were grown using the vapor phase chemical transport technique at a growth temperature of 950°C. The CdSe and CoSe previously sintered were introduced in the adequate proportions in weight into a quartz ampoule with iodine as the transport agent.

The TR setup is as follows: as heating element we used a  $\text{SnO}_2$ -covered glass slide, with the sample mounted onto this conducting glass. An AC current of about 1 A was applied through the thin oxide layer with a frequency of 11 Hz. Glass slide and sample were mounted on a copper heat sink. The light from a SPEX monochromator attached to a tungsten lamp was focused onto the sample and the reflected light was detected by a Si pin photodiode. Phase sensitive techniques for light detection were

used through an EG & G 5210 lock-in amplifier tuned to heating frequency. In Fig. 1 we show a block diagram of the thermoreflectance setup.

### 3. Results and discussion

In the thermoreflectance technique, when a temperature change is applied to the sample, the fundamental optical properties are changed; in particular, if the sample temperature is increased, it can be easily shown that the optical band edge shifts to lower energies. The band gap decreases as the temperature does. So, if we modulate the sample temperature, we will be modulating the absorption band edge, and in particular, we will be modulating the reflectivity spectrum of the material. It can be shown that since this modulation method does not destroy the translational symmetry of the material, the complex dielectric function change induced by the temperature modulation has a first derivative character:

$$\Delta \varepsilon = \frac{\partial \varepsilon}{\partial T} \Delta T = \left[ \frac{\partial \varepsilon}{\partial E_g} \frac{\partial E_g}{\partial T} + \frac{\partial \varepsilon}{\partial \Gamma} \frac{\partial \Gamma}{\partial T} \right] \Delta T,$$

where  $E_g$  is the band gap energy and  $\Gamma$  is a phenomenological broadening parameter which is

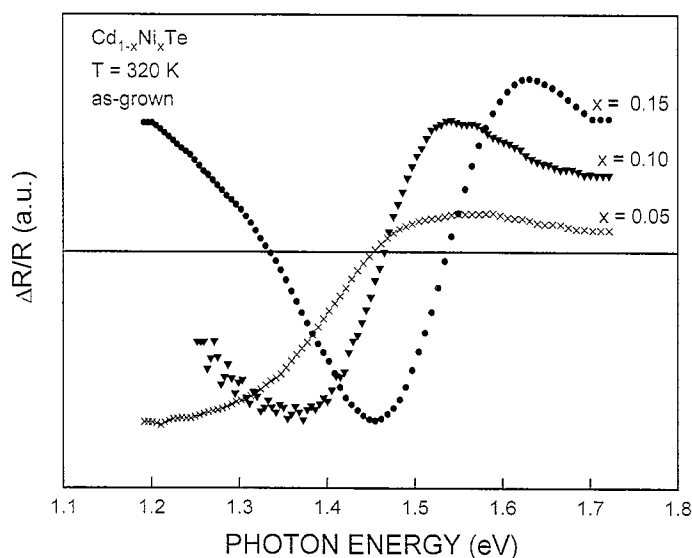


Fig. 2. Thermoreflectance spectra for the  $\text{Cd}_{1-x}\text{Ni}_x\text{Te}$  thin films with different Ni concentrations. The lineshape is that of an oscillation at the fundamental band gap energy that occurs at the  $\Gamma$ -point in the Brillouin zone.

related to dispersive mechanisms such as poor crystalline quality, disorder, etc.

The TR spectra for the  $\text{Cd}_{1-x}\text{Ni}_x\text{Te}$  thin films with different concentrations are shown in Fig. 2. First, it can be observed a very clear shift of the TR lineshape to higher energies as the Ni concentration in the film increases. By adjusting the theoretical lineshape to the experimental data, we have obtained the following values for the fundamental band gap transition ( $E_0$ -point): 1.42 eV ( $x = 0.05$ ); 1.46 eV ( $x = 0.10$ ); and 1.54 eV ( $x = 0.15$ ). We have interpreted this blue-shift in the band gap as due to a quantum-size effect produced by the nanocrystalline nature of the grains in the films; when the grain size becomes comparable to the exciton Bohr radius there appear quantized levels in both the conduction and valence bands, and these levels are responsible for the quantum-confinement effects [9]. We also believe that there could be a contribution to this energy shift coming from an alloying effect due to the formation of the  $\text{Cd}_{1-x}\text{Ni}_x\text{Te}$  ternary compound. In Fig. 2 it can be also observed that the lineshape for the TR spectrum corresponding to the sample with a Ni concentration of 5 at% is much broader than the

other two, meaning that the broadening parameter,  $\Gamma$ , is larger as a result of a lower crystalline quality film. For the film with a Ni concentration of 15 at% there appears to be a slight shoulder at an energy of around 1.30 eV which could be due to a deep level transition; studies to elucidate the nature of these deep levels are under way and will be published elsewhere.

For the  $\text{Cd}_{1-x}\text{Co}_x\text{Te}$  system, in Fig. 3 we show the TR spectra for those crystals having Co concentrations of 1 at% and 5 at%. The TR spectrum for the  $\text{Cd}_{0.99}\text{Co}_{0.01}\text{Se}$  sample shows a very well defined and sharp oscillation at an energy of around 1.68 eV that corresponds to the fundamental band gap transition. A higher energy transition is observed at 2.12 eV which should correspond to the spin-orbit splitting. Baranovski et al. [10] determined the energy band diagram for the energy levels of  $\text{Co}^{2+}$  ( $d^7$ )-impurities, showing that the corresponding energies for transitions between the  $^4A_2$  ground state and the triplet  $^4T_1$  were, at room temperature: 1.65, 1.58 and 1.50 eV. These transitions are observed in the TR spectrum of the  $\text{Cd}_{0.99}\text{Co}_{0.01}\text{Se}$  crystal, and they are much well defined in the spectrum corresponding to

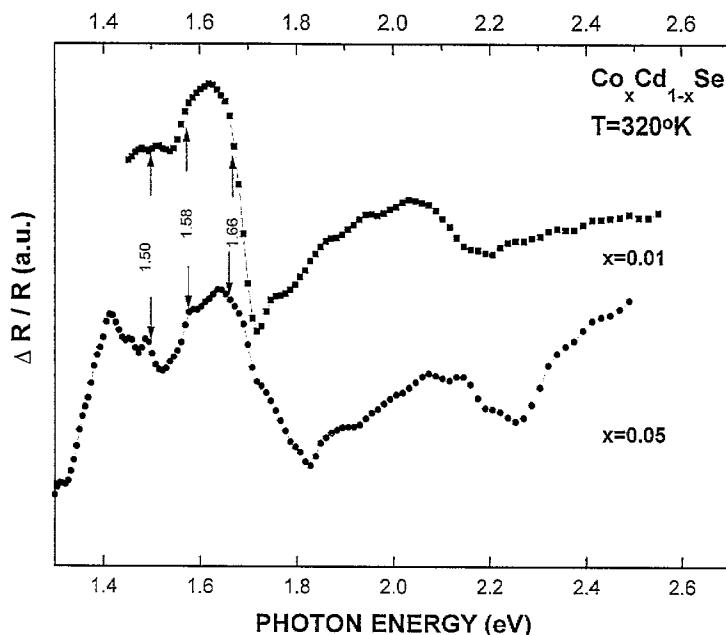


Fig. 3. Thermoreflectance spectra for the  $\text{Cd}_{1-x}\text{Co}_x\text{Se}$  crystals. The energies at 1.50, 1.58 and 1.65 eV correspond to the transitions between the  $^4A_2$  ground state of the  $\text{Co}^{2+}$  ion and the split levels of the triplet  $^4T_1$ .

the  $\text{Cd}_{0.95}\text{Co}_{0.05}\text{Se}$  sample. For this last crystal, the main oscillation corresponding to the  $E_0$ -point is located at an energy of about 1.73 eV, and the oscillation related to the spin-orbit splitting is at 2.18 eV.

The values obtained from the TR spectra for the fundamental band gap are smaller than the values for the band gap of the parent compound CdSe which is 1.75 eV at room temperature. Up to date, we have not found results on the stoichiometry dependence of the band gap,  $E_g(x)$ , for the ternary semiconductor  $\text{Cd}_{1-x}\text{Co}_x\text{Se}$ . Our results suggest that for small  $x$ -values there is a decrease in the band gap energy of the compound as the Co concentration increases, and so the Vegard's law is not followed by this compound in the range of small  $x$ -values; it is possible that as we move to higher values of  $x$ ,  $E_g(x)$  could start to increase with  $x$ , showing a 'bowing' behavior.

As we already stated, this ternary DMS crystalizes in the wurzite structure and so we would expect to observe the splitting of the light hole and heavy hole valence bands due to the lack of symmetry. In our TR spectra it is difficult to establish if such additional transition is present. It could be that the shoulder observed slightly above the band gap would correspond to such conduction band–light hole valence band transition.

#### 4. Conclusions

In summary, in this paper we have presented results on the characterization, using the thermoreflectance spectroscopy, of the optical transitions in two types of diluted semimagnetic semiconductors:  $\text{Cd}_{1-x}\text{Ni}_x\text{Te}$  thin films and  $\text{Cd}_{1-x}\text{Co}_x\text{Se}$  crystals. For the CdNiTe films we found that the transition corresponding to the  $E_0$ -point energy shows a blue-shift as the Ni concentration in the film increases; that is, as the film crystalline grain size decreases.

This behavior can be consistently interpreted in terms of quantum confinement size effects due to the nanometer-sized of the grains in the different films. For the CdCoSe crystals, the TR spectra gave us the result that, for low Co concentrations, the band gap energy decreases as the Co content increases, contrary to the usual behavior in forming semiconductor alloys which obey Vegard's law. For these DMS crystals we also observed transitions below the band gap which agree quite well with those expected as the result of the additional levels introduced by the  $\text{Co}^{2+}$  ions when they enter into the hexagonal CdSe lattice.

#### Acknowledgements

We acknowledge the partial financial support of COLCIENCIAS-Colombia and CONACYT-Mexico.

#### References

- [1] W. Giriat, J.K. Furdyna, *Semicond. Semimet.* 25 (1988) 1.
- [2] U. Kaufmann, J. Windscheif, G. Brunthaler, *J. Phys. C: Solid State Phys.* 19 (1984) 6169.
- [3] O. Alvarez-Fregoso, J.G. Mendoza-Alvarez, O. Zelaya-Angel, F. Morales, *J. Appl. Phys.* 80 (1996) 2833.
- [4] M. Villeret, S. Rodriguez, E. Kartheuser, *Phys. Rev. B* 41 (1990) 10028.
- [5] M. Villeret, S. Rodriguez, E. Kartheuser, *Phys. B* 162 (1990) 89.
- [6] A. Lewicki, A.I. Schindler, Y. Miotkowski, J.K. Furdyna, *Phys. Rev. B* 41 (1990) 4653.
- [7] H. Ariza-Calderon, J.G. Mendoza-Alvarez, F. Sanchez-Sinencio, O. Alvarez-Fregoso, A. Lastras-Martinez, G. Ramirez-Flores, *J. Appl. Phys.* 74 (1993) 5154.
- [8] O. Alvarez-Fregoso, O. Zelaya-Angel, J.G. Mendoza-Alvarez, F. Sanchez-Sinencio, M.H. Farias, L. Cota-Araiza, *J. Phys. Chem. Solids* 56 (1995) 117.
- [9] O. Alvarez-Fregoso, J.G. Mendoza-Alvarez, O. Zelaya-Angel, *J. Appl. Phys.* 82 (1997).
- [10] J.M. Baranovski, J.M. Langer, S. Stefanowa, in: *Proc. 11th Int. Conf. on the Physics of Semiconductors*, Warsaw, Poland, 1972, p. 1001.