QUANTUM CONFINEMENT EFFECTS IN NANOCRYSTALLINE GaAs FILMS GROWN BY R.F. SPUTTERING

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ABSTRACT

GaAs thin films were grown on Corning glass slides by using the r.f. sputtering deposition technique, and a GaAs single crystal as the target. In order to control the grain size of the microcrystals in the film we changed three main parameters in the deposition system: growth time, gas pressure and the substrate temperature. The different sets of samples were analyzed by X-ray diffractometry, and from the peak width in the diffractograms we were able to obtain the mean grain sizes in the films which were in the range between about 8 and 15 Å. The absorption spectra for these films were measured by light transmission with an standard spectrophotometer; and also using the photoacoustic (PA) technique. In the spectra obtained by PA spectroscopy it was clearly observed the bands due to transitions between quantized levels arising because of the quantum confinement effects taking place in the GaAs nanocrystals. From these measurements it was also evident the blue shift of the bandgap energy, ΔE_g , due to these quantum effects. We show the dependence of ΔE_g on the nanocrystal size and compare it with different models of quantum confinement.

RESUMEN

Se crecieron películas delgadas de GaAs sobre sustratos de vidrio corning usando la técnica de deposición r.f. sputtering, y un cristal simple de GaAs como blanco. Con el fin de controlar el tamaño de grano de los microcristales en la película cambiamos tres parámetros importantes en el sistema de deposición: tiempo de crecimiento, presión del gas y la temperatura del sustrato. Los diferentes conjuntos de muestras fueron analizadas por difractometría de rayos X, y del ancho del pico más alto en los difractogramas se estimaron los tamaños medios de grano en las películas, los cuales estuvieron entre 8 y 15 Å. El espectro de absorción para estas películas fue medido por transmisión de luz con un espectrofotómetro estándar, y también usando la técnica fotoacústica (FA). En los espectros obtenidos por espectroscopia FA se observaron claramente bandas debidas a transiciones entre niveles cuantizados que se presentan como efectos de confinamiento cuántico que toman lugar en los nanocristales de GaAs. De estas medidas fue evidente también el corrimiento hacia el azul de la energía de banda prohibida, ΔE_g, debido a dichos efectos cuánticos. Se muestra la dependencia de ΔE_g con el tamaño del nanocristal y se compara con diferentes modelos de confinamiento cuántico.

INTRODUCTION

In the search for materials with new properties, the development of nanocrystals with typical dimensions in the range 10-500 Å has open a new and wide field of applications because of the changes in the fundamental properties of matter that take place when the electrons are confined to such nanometric scale.

For example, for CdS it has been shown that the band gap energy can be tuned in a broad energy range between 2.5 and 4.5 eV by changing the nanocrystal grain size; the radiative lifetime change from tens of a picosecond up to several nanoseconds; and also the fusion point raises from 400 ^{o}C up to 1600 ^{o}C.

For semiconductor nanocrystals, the huge variation in their optical properties is due to the so-called quantum confinement, which occurs when the nanocrystals dimensions are of the order of the exciton Bohr radius. When this happens the density of states is quantized and the permitted energy levels will depend on the size of the nanocrystals.

The III-V semiconductors are good candidates to exhibe a strong quantum confinement because of their intermediate Exciton Bohr radius which oscillates between 100 Å for InP and 140 Å for GaAs. So, our objetive is to grow GaAs nano-crystals in order to observe quantum confinement and the shift of the bandgap energy with the crystalite size.

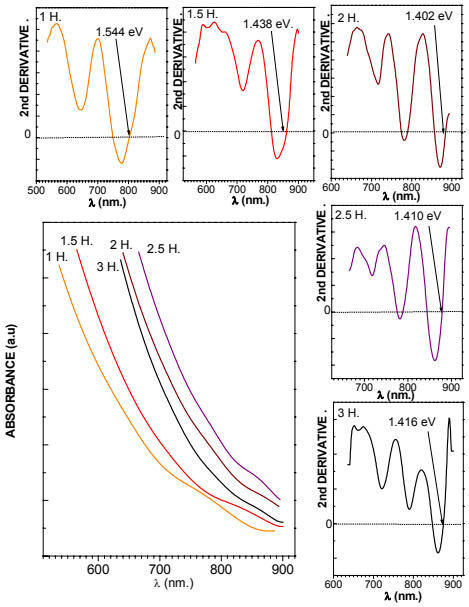

Fig.1 Optical spectra of GaAs films. The inset illustrates the second derivative of the optical absorption curves. The intersection with wavelengths axis determines the absorption edge.

EXPERIMENTAL

The GaAs films were grown by r.f magnetron sputtering technique with a GaAs single crystal wafer of 2 inches as the target. As substrate, 7059 Corning glass slides were employed. Three series of five films each one, were grown changing the parameters: gas pressure (Argon), substrate temperature and growth time respetively.

The crystalline structure and film grain size were resolved through X-ray diffraction (XRD) patterns using a X-ray diffractometer SIEMENS D5000 (Cu K_α line). Optical absorption spectra were obtained in a Unicam 8700 UV/VIS spectrophotometer in the range 500–900 nm. The optical absorption were measured too with the photoacoustic technique, using chopped light from xenon lamp (700 W) through monocromator and then crossing a optical fiber for impinge on the sample in the photoacoustic cell. The photoacoustic signal from a microphone inside acoustic cell is leaded to a lock-in amplifier SR530 and finally read for a p.c.

In this case all samples are optically transparent, therefore according to Rosencwaig'theory, the PA signal is proportional to the absorption coefficient, and since this signal is concerned with the amount of absorbed light instead of the reflected or transmitted light, the influence of light scattering effects is greatly reduced, which make of this technique a powerful tool to observe the changes in the absorption spectra due to the redistribution in the density of states by quantum confinement effects.

RESULTS AND DISCUSSION

As observed from the XRD patterns there appears a broad diffraction peak centered at around 27º corresponding to the GaAs (111) direction, and from the peak FWHM we could estimate the average nanometer grain size to be in the range 9-13 Å. A larger variation and bigger crystallites are obtained when the growth time is changed between 1 and 3 hours. Changing the Ar pressure and the substrate temperature also influences on the film grain sizes.

Fig.1 show the optical absorption spectra measured by spectrophotometry show a clear shift of the absorption edge to lower energies as the growth time increases and consequently the grain size increases. By taking the 2nd derivative of the absorption curve and observing where it is zero we could obtain an approximate value of the bandgap energy.

When the same set of GaAs films were measured by PA spectroscopy, the spectra show some very well defined oscillations which correspond to the transitions between the quantized energy levels in the valence and conduction bands as shown in Fig.2. In the insets are shown the plots of $(\text{PA signal}*E)^2$ vs. E which are related to direct transitions between parabolic bands, and it can be observed that there exist a region of linear behaviour, and from a linear fitting in this region, the band gap values were obtained, which are in agreement to those obtained from the optical absorption measurements.

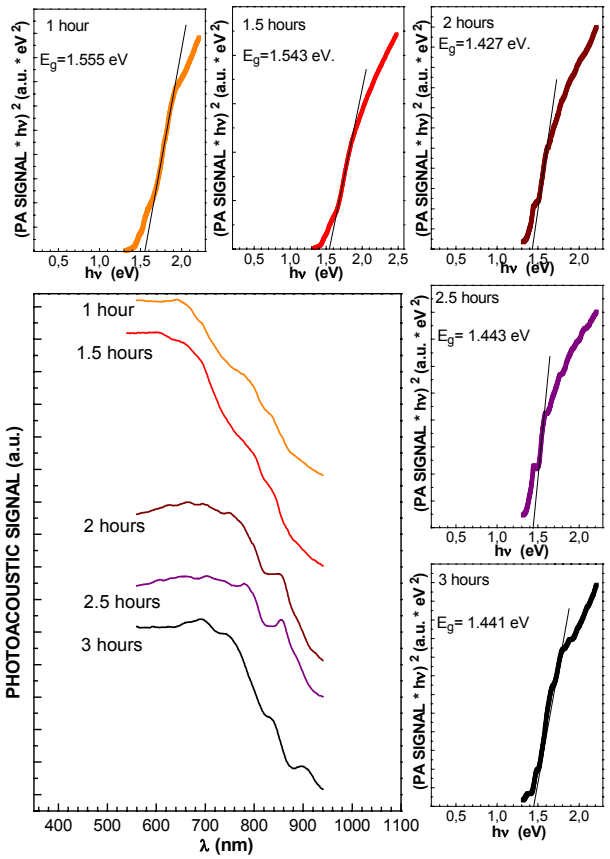

Fig. No. 2 Photoacoustic (PA) intensity spectra of nanocrystalline GaAs films with different grain size. The inset plots illustrates the (signal PA *hν)^2 vs. hν. The values of the corresponding optical band gap are estimated by extrapolation of an apparently narrow linear region.

The maximum bandgap energy shift obtained, ΔEg=0.314 eV, was for a sample grown at a substrate temperature of 100 ^oC for which the grain size estimated from the XRD pattern was of about 7.5 Å.

The grain size and absorption edge experimental values, obtained for the different conditions of grown, are shown in the table 1.

Table 1. Experimental values obtained for different conditions of the growth.

Time (hours)	Grain size (Å)	Absorption edge (eV.)	ΔE_g (eV.)
1	9.17	1.555	0.131
1.5	9.8	1.543	0.119
2	10.13	1.427	0.003
2.5	11.33	1.443	0.019
3	12.58	1.441	0.017
Pressure (mTorr)	Grain size (Å size (Å	Absorption edge (eV.)	ΔE_g (eV.)
1	11.53	1.421	-0.003
5	10.82	1.427	0.003
10	9.21	1.459	0.035
15	9.08	1.543	0.119
20	9.8	1.547	0.123
Temperature (^{0}C)	Grain size (Å)	Absorption edge (eV.)	ΔE_g (eV.)
100	7.49	1.738	0.314
150	8.25	1.686	0.262
200	8.59	1.581	0.157
250	8.28	1.533	0.109
300	10.31	1.480	0.056

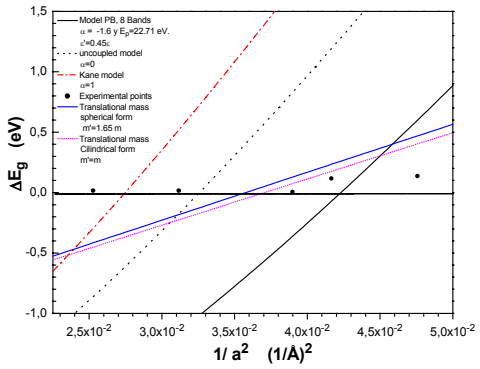

Fig. No. 3 Quantum-confined shift of the fundamental edge of the nanocrystalline GaAs films grown changed time of deposition, as a function of the inverse average crystal radios squared.

The fig. 3 show the absorption edge shift as function of a^{-2}, where a is the average radius of the nanocrystals. Is possible observer in this plot the increasing of the absorption edge with the decreasing in the grain average size. We used the parabolic bands approximation model and the bands eight model, finding that is necessary an increasing in the effective mass and the dielectric constant for this models, respectively. For the bands eight model were found that the α parameter, associated with the contribution of higher bands to the electron effective mass have a value of –1.6 when the non parabolicity parameter is E_p=22.71 eV, as is reported for the GaAs.

In the parabolic band approximation model, we take into a count spherical and cylindrical forms for the nanocrystals, as show the fig. 3 for the first model the increasing in the effective mass (1.65 times the bulk effective mass) have to be grater than the increasing considering the cylindrical form.

The bands eight model, in which takes in count both the coupling of conduction and valence bands and the complex structure of the valence band in nanocrystals with a infinite potential barrier, is necessary take the dielectric constant to be 0.45 times the of bulk for obtain a good agreement with experimental points corresponding to the smaller grain sizes. This can be mean that there are ranges for apply this model, and their special cases (Kane model and uncoupled model).

CONCLUSION

Were grown nanocrystallines GaAs films, the quantum confinement effects were best observed with the photoacoustic technique, because this technique avoids the light scattering. With it same technique we found that the absorption edge shift lightly to the blue with the decreasing in the grain size. This behaviour can be explained using the parabolic band approximation with a effective mass greater than the of bulk, or the bands eight model considering to a dielectric constant smaller than the of bulk.

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REFERENCES

[1] A. Rosencwaig, A. Gersho. Journal of Applied Physics. Vol. 47, No.1, 64(1976).
[2] Z. Yasa, W. Jackson, N. Amer, Appl. Opt. 21 (1982).
[3] Q. Shen, K. Abe. T. Shigenari, T. Toyoda, Journal of Luminiscence 87-89, 444(2000).
[4] J. I. Pankove. Optical processes in semiconductors. (Dover publications, inc, 1971), p. 34-106.
[5] Al. L. Efros and A. L. Efros. Sov. Phys. Semicond. Volume 16(7), 772(1982).
[6] Al. L. Efros and M. Rosen. Physical Review B, volume 58, number 11, 7121(1998).
[7] Geral Bastard. Halsted Press, JHON WILEY & SONS, Inc, (1988), p.p. 237-300.