Superficies y Vacío **18(3)**, 1-3 ,septiembre de 2005 ©Sociedad Mexicana de Ciencia y Tecnología de Superficies y Materiales

Characterization by photoreflectance of E_0´ and E_1 silicon-like critical points in ion implanted $Si_{1-y}C_y$ thin films

M. Melendez-Lira
Physics Department, Centro de Investigación y de Estudios Avanzados del IPN,
Apartado Postal 14-740, 07000 Mexico, D. F., México.
(Recibido: 10 de julio de 2005; Aceptado: 11 de agosto de 2005)

The dependence of E_0´ and E_1 critical points energies with carbon content in $Si_{1-y}C_y$ thin films grown by ion implantation and crystallization have been obtained by room temperature photoreflectance spectroscopy. We present results from samples crystallized by solid phase epitaxy and laser annealing. We found that the E_0´ values depend on the crystallization procedure. For solid phase epitaxy crystallization, E_0´ initially increases up to 20 meV for y=0.003 then decreasing to values near that of silicon for y =0.014. While for laser annealing the E_0´ values are always lower than that of silicon. E_0´ shows a behavior far from that predicted by the virtual crystal approximation and deformation potential theories. E_1 shows a continuous increase as function of the carbon content, this is reasonably well described using the aforementioned theories.

Keywords: Semiconductor alloys; $Si_{1-y}C_y$; Photoreflectance

1. Introduction

Group IV alloys are very interesting from both the theoretical and experimental points of view. However, until now $Si_{1-x}Ge_x$ and SiC are the only group IV alloys used in the production of devices [1,2] The $Si_{1-y}C_y$, $Ge_{1-y}C_y$ and $Si_{1-x-y}Ge_xC_y$ systems are very attractive because the possibility of band gap modulation between theband gap values of Si and/or Ge and C,[3] several growth techniques have been employed to produce thin films of these alloys [4-10]However there are problems to overcome before samples of very good quality can be obtain. Besides the huge difference in atomic radii between Si and C there is the low solubility problem of C in Si. The first problem above mentioned is also an opportunity to stress-taylor the electronic and structural properties of $Si_{1-x-y}Ge_xC_y$ samples, but a good deal of work is still required.

There are a couple of studies about the E_0' and E_1 critical points in $Si_{1-y}C_y$ alloys carried out on molecular beam epitaxy grown samples in which low temperature electroreflectance and room temperature ellipsometry are employed as characterization techniques[13,14]. But until our knowledge this is the first photoreflectance study. Photoreflectance is a well stablished characterization espectroscopy, some interesting features are its contactless character, the straightforward determination of critical points energies and its great sensitivity to sample quality.

2. Experimental details

The studied samples were grown by C ion implantation on Si(001) substrates and crystallized by solid phase epitaxy or laser annealing. Multiples of 1 x10^{15} C^+/cm^2 at 25 KeV were utilized to produce samples with peak concentrations of 0.026, 0.091,1.17, 1.43 and 1.82 at. %, samples #4, #7, #9, #13 and #15 respectively. After implanted the samples were subject to solid phase epitaxy to crystallization. The other set studied was prepared under similar C implantation conditions and peak concentrations between 0.35 and 3.5 at. % C were obtained, laser annealing was employed for crystallization.[15]. We only studied the samples with 0.7, 1.4 and 2.1 at. % C, samples 4d, 6m and 2a respectively. For both sets the peak concentration was determined by secondary ion mass spectroscopy (SIMS). A standard photoreflectance (PR) setup was employed with an 8 mW HeNe laser as excitation beam.

3. Results and discussion

Figure 1, shows the room temperature PR spectra from the two sets studied. Several scans were averaged to increase the ratio signal to noise. It is worth to mention that we could not obtain a good PR spectrum from a piece of silicon similar to the silicon substrate employed in the implantation, we neither obtain any signal from the E_2 silicon-like critical point transition. The ratio signal to noise for sample 2a, laser annealed, was too low to yield any useful information.

The E_0´ and E_1 critical points energies are very close, but it is apparent in Fig. 1 that there is a slight change in the PR line as we go from samples #4 to #15. The PR spectra for samples 4d and 6m confirm beyond any doubt that the change comes from a separation of the PR signals coming from the E_0´ and E_1 critical points. In order to obtain the energy of the transitions involved we fitted our PR spectra to the theoretical third-derivative functional form from Aspnes' theory considering a 3 dimensional critical point for both E_0´ and E_1 [16]. The fittings are shown along with the experimental results in Fig.1 and the energies obtained are presented in Table I. Because the good agreement of our fittings with the experimental spectra it seems that the use of a 3-dimensional critical point to describe these PR features is adequate.

Figure 2a presents the dependence of the E_0´ and E_1 critical points energies as function of the peak carbon concentration. The samples crystallized by laser annealing

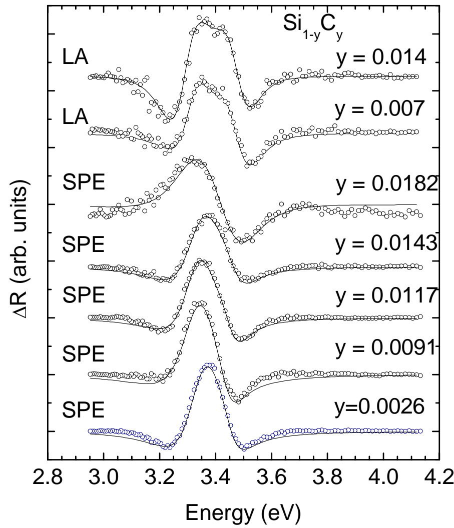

Figure 1. Room temperature photoreflectance spectra for $Si_{1-y}C_y$ thin films. Symbols represent the experimental spectra, continous line correspond to fittings using Aspnes' third derivative line form.

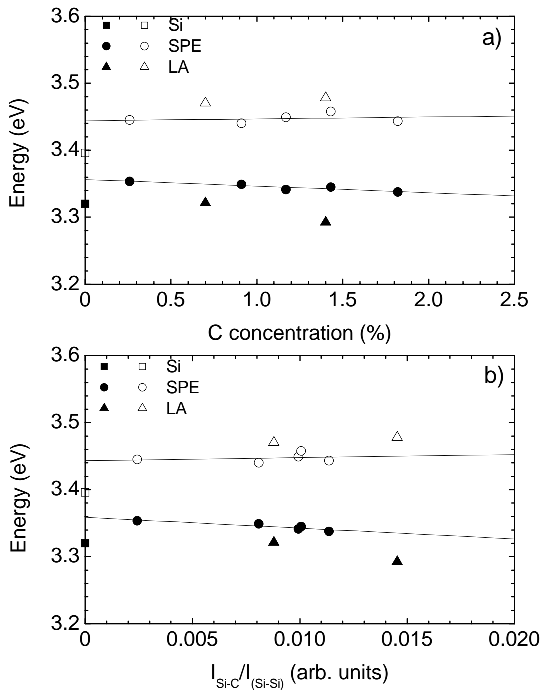

Figure 2. a) E_0' and E_1 critical points for $Si_{1-y}C_y$ thin films as function of carbon peak concentration. Solid symbols correspond to E_0' values while empty ones to E_1 values. b) E_0' and E_1 critical points for $Si_{1-y}C_y$ thin films as function of substitutional carbon as obtained from Raman spectroscopy. In both figures the squares represent values for silicon E_0' and E_1 critical points. MBE, SPE and LA are refered to the growth procedure and stands for molecular beam epitaxy, solid phase epitaxy and laser annealed respectively.

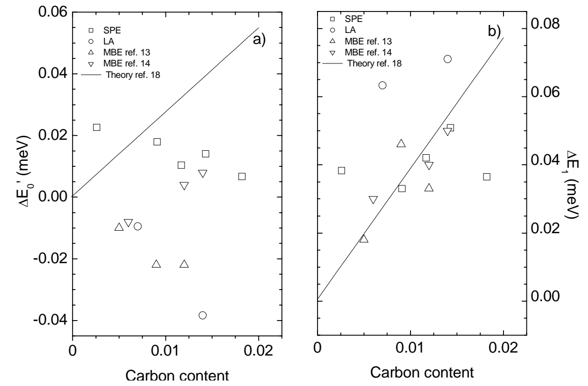

Figure 3. a) E_0' critical point shift for $Si_{1-y}C_y$ thin films as function of carbon peak concentration. b) E_1 critical point shift for $Si_{1-y}C_y$ thin films as function of carbon peak concentration. MBE, SPE and LA are refered to the growth procedure and stands for molecular beam epitaxy, solid phase epitaxy and laser annealed respectively.

do not follow the trend found for the solid phase epitaxy recristallized set. Because of the low solubility of carbon in silicon, the amount of substitutional carbon will depend strongly on the characteristics of growth. It is important to have present that only substitutional carbon will determine alloy properties. A possible explanation for the different behavior of E_0' and E_1 between both sets of samples is a discrepance between the peak concentration obtained by SIMS and the real amount of substitutional carbon. It is found that in CVD grown $Si_{1-x-y}Ge_xC_y$ the substitutional carbon content as measured by Rutherford backscattering spectrosopy channeling is only a fraction of the nominal carbon content[17]. Then, in order to evaluate at what extent the differences found by photoreflectance spectroscopy are due to the different rate in the incorporation of carbon in silicon lattice sites a direct determination will be needed. An approach used in silicon with low carbon content to determine the amount of substitutional carbon involves the use of infrared spectroscopy. However it is not useful when high amounts of carbon are present. Raman spectroscopy is an interesting alternative because substitutional carbon in silicon produce a Raman active local mode. The ratio between Si-C and Si-Si Raman peaks areas has a direct correlation with the amount of substitutional carbon. A similar comparison between Si-Si and Si-C modes is not possible using infrared spectroscopy because the Si-Si mode is infrared inactive. Figure 2.(b) presents the dependence of the E_0' and E_1 critical points energies as function of the ratio between Si-C and Si-Si Raman peaks areas[18]. Even when Raman spectroscopy shows that laser annealed samples have a higher amount of substitutional carbon than solid phase epitaxy samples, the E_0' and E_1 trends remain unchanged. Figures 3.(a) and 3.(b) present the shifts of E_0' and E_1, referred to silicon, obtained by PR along with results obtained by electroreflectance and ellipsometry in MBE grown

Table 1. E_0' and E_1 critical energies for $Si_{1-y}C_y$ thin films as obtained from fitting to photoreflectance spectra. SPE and LA stands for solid phase epitaxy and laser annealed respectively.

Sample	Crystallization procedure	y	E_0' (eV)	E_1 (eV)
#4	SPE	0.0026	3.354(6)	3.445(3)
#7	SPE	0.0091	3.348(9)	3.440(0)
#9	SPE	0.0117	3.341(3)	3.449(0)
#13	SPE	0.0143	3.345(0)	3.457(8)
#15	SPE	0.0182	3.337(3)	3.443(5)
4d	LA	0.007	3.321(5)	3.470(3)
6m	LA	0.014	3.292(7)	3.478(0)

y: carbon peak concentration

samples as taken from literature[13, 14]. We employed the values E_0'(Si)= 3.331 eV and E_1 (Si) = 3.407 eV for silicon critical points in order to calculate the shift values obtained from PR [19]. The theoretical analysis employing the virtual crystal approximation and potential deformation theory carried out by Zollner is also included in figures 3.(a) and 3.(b). The E_0' results have a behavior completely different to that predicted by the theoretical analysis. Something interesting is that apparently there are two different trends for each set of samples. Both showing a decreasing trend in the E_0' values. This could be explained taken in account the different growth kinetics between solid phase epitaxy, MBE and laser annealed crystallization. Apparently the E_1 shifts are described reasonably well by the combination of the virtual crystal approximation and potential deformation theory. Our results could suggest that a closer analysis for the deformation potential values for the E_0' critical point is needed.

4. Conclusions

Photoreflectance spectroscopy results for E_0' and E_1 critical point energies in $Si_{1-y}C_y$ thin films agree with those obtained by low temperature electroreflectance and room temperature ellipsometry. It is clear that more theoretical and experimental work is needed to understand the behavior of the E_0' critical point in $Si_{1-y}C_y$ alloys. On the other hand the E_1 behavior is reasonably well described by the combination of virtual crystal approximation and deformation potential theory. The discrepances in the behaviour of E_0' and E_1 suggest that the E_0' critical point is more sensitive to sample's growth details.

References

[1] J.C. Bean, proceedings of IEEE **80**, 571(1992), *and references therein.*

[2] H. Morkoç, S. Strite, G.B. Gao, M.E. Lin, B. Sverdlov and M. Burns. J. Appl. Phys. **76**, 1363 (1994).

[3] R.A. Soref, J. Appl. Phys. **70**, 2470 (1991).

[4] J.B. Posthill, R.A. Rudder, S.V. Hattangady, G.G. Fountain and R.J. Markunas. Appl. Phys. Lett. **56**, 734 (1990).

[5] S.S. Iyer, K. Eberl, M.S. Goorsky, F.K. LeGoues, J.C. Tsang and F. Cardone. Appl. Phys. Lett. **60**, 356 (1992).

[6] J.W. Strane, H.J. Stein, S.R. Lee, B.L. Doyle and S.T. Picraux. Appl. Phys. Lett. **63**, 2786 (1993).

[7] P. Boucaud, C. Francis, F.H. Julien, J.-M. Lourtioz, D. Bouchier, S. Bodnar, B. Lambert and J.L. Regolini. Appl. Phys. Lett. **64**, 875 (1994).

[8] Z. Atzmon, A.E. Bair, E.J. Jaquez, J.W. Mayer, D. Chandrasekhar, D.J. Smith, R.L. Hervig and M. Robinson. Appl. Phys. Lett. **65**, 2559 (1994).

[9] W. Faschinger, S. Zerlauth, G. Bauer and L. Palmetshofer. Appl. Phys. Lett. **67**, 3933 (1995).

[10] J. Mi, P. Warren, P. Letourneau, M. Judelewicz, M. Gailhanou and M. Dutoit. Appl. Phys. Lett. **67**, 259 (1995).

[11] J. Kolodzey, P.A. O'Neil, S. Zhang, B.A. Orner, K. Roe, K.M. Unruh, C.P. Swann, M.M.White and S.I. Shah. Appl. Phys. Lett. **67**, 1865 (1995).

[12] M. Todd, P. Matsunaga, J. Kouvetakis, D. Chandrasekhar and D.J. Smith. Appl. Phys. Lett. **67**, 1247 (1995).

[13] W. Kissinger, M. Weidner, H.J. Osten, and M. Eichler. Appl. Phys. Lett. **65**, 3356(1994).

[14] S. Zollner, C.M. Herzinger, J.A. Woollam, S.S. Iyer, A.P. Powell, and K. Eberl, Solid State Commun. **96**, 305(1995).

[15] K.M. Kramer, and M.O. Thompson. J. Appl. Phys. **79**, 4118(1996).

[16] D.E. Aspnes, Surf. Sci. **37**, 418(1973).

[17] R.J.C.S Sego, A.E. Bair, and T.L. Alford. Materials Chemistry and Physics 46, 283(1996) .

[18] M. Melendez-Lira, J. Menendez, K. M. Kramer, M. O. Thompson, N. Cave, R. Liu, J. W. Christiansen, N. D.Theodore, and J. J. CandelariaJ. Appl. Phys**. 82**, 4246(1997).

[19] S. Zollner. J. Appl. Phys. **78**, 5209(1995).