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# SPECTROSCOPIC ELLIPSOMETRY AND BAND STRUCTURE OF $\text{Si}_{1-y}\text{C}_y$ ALLOYS GROWN PSEUDOMORPHICALLY ON Si (001)

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## ABSTRACT

We have measured the dielectric functions of three  $\text{Si}_{1-y}\text{C}_y$  alloys layers ( $y \leq 1.4\%$ ) grown pseudomorphically on Si (001) substrates using molecular beam epitaxy at low temperatures. From the numerical derivatives of the measured spectra, we determine the critical point energies  $E'_0$  and  $E_1$  as a function of  $y$  ( $y \leq 1.4\%$ ) using a comparison with analytical line shapes and analyze these energies in terms of the expected shifts and splittings due to negative hydrostatic pressure, shear stress, and alloying. Our data agree well with the calculated shifts for  $E_1$ , but the  $E'_0$  energies are lower than expected. We discuss our results in comparison with recent tight-binding molecular dynamics simulations by Demkov and Sankey (Phys. Rev. B 48, 2207, 1993) predicting a total breakdown of the virtual-crystal approximation for such alloys.

## INTRODUCTION

Recent years have seen tremendous progress in the epitaxial growth of group-IV semiconductor alloys.<sup>1</sup> Using  $\text{Si}_{1-x}\text{Ge}_x$  alloys, it has become possible to create heterojunction bipolar transistors that outperform traditional silicon technology, yet remain compatible with standard manufacturing methods.<sup>2,3</sup> Most physical properties, particularly the band structure, of such  $\text{Si}_{1-x}\text{Ge}_x$  alloys can be described with reasonable accuracy by what has become known as the virtual crystal approximation:<sup>4-6</sup> A virtual atom with average properties (taking into account the composition) is placed at each lattice site. The crystal properties are then calculated from this virtual crystal, usually resulting in a linear interpolation between the two end points (Si and Ge), with a small quadratic correction term resulting in a slight bowing of the curve. There are important exceptions to this rule, for example the three-mode behavior of

the optical phonons<sup>7</sup> due to their narrow band width (small dispersion) or the composition dependence of the lowest band gap<sup>8</sup> due to the crossover from a Si-like to a Ge-like band structure, but these are well understood. Deviations of the lattice constant from Vegard's law are very small.<sup>9</sup>

For a variety of technical reasons, particularly to reduce<sup>10</sup> the built-in strain in the layers (or adjust it to a desired value), it is also desirable to incorporate carbon into such materials and form  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys. Such structures have been produced by a number of groups during the past years.<sup>11,12</sup> In particular,  $\text{Si}_{1-y}\text{C}_y$  alloys can be grown pseudomorphically on Si (001) with a carbon content of up to 2% and a thickness of up to about 200 nm. At larger compositions and thicknesses, the layers relax through formation of misfit dislocations.<sup>13</sup>

After growth, the pseudomorphic structures were studied with a variety of techniques, including transmission electron microscopy, secondary-ion mass spectroscopy, x-ray scattering, Rutherford backscattering, and Raman spectroscopy.<sup>14</sup> All evidence suggested that these  $\text{Si}_{1-y}\text{C}_y$  alloys had physical properties very similar to the very well studied  $\text{Si}_{1-x}\text{Ge}_x$  alloys. In particular, the Raman signal could be interpreted with a simple mass defect, i.e., a carbon atom located at a silicon lattice site.<sup>14</sup> No indications about imperfections in the alloy structure could be detected. At the time, the band structure of these alloys remained unknown, since their photoluminescence signal<sup>15</sup> was very weak, presumably due to a large number of nonradiative recombination centers. Nevertheless, the issue of determining the band structure experimentally did not seem worthy of pursuing. Instead, it was assumed at the time that the band structure of free-standing  $\text{Si}_{1-y}\text{C}_y$  alloys was similar to  $\text{Si}_{1-x}\text{Ge}_x$  alloys, i.e., that all bands would increase linearly with increasing carbon composition. Because of the built-in strain in pseudomorphic samples all bands are split, therefore the lowest (indirect) band gap in  $\text{Si}_{1-y}\text{C}_y$  alloys was expected to be smaller than the band gap of the silicon substrate.

The situation became more interesting after a theory paper by Demkov and Sankey.<sup>16</sup> Their tight-binding molecular-dynamics simulations predicted a total breakdown of the virtual-crystal approximation for  $\text{Si}_{1-y}\text{C}_y$  alloys, due to a microscopic relaxation of the lattice around the Si impurities. Therefore, we decided to study the band structure of  $\text{Si}_{1-y}\text{C}_y$  alloys in more detail. It is well known that the lowest band gap is often studied with photoluminescence. As mentioned earlier, however, the samples under investigation here did not display a significant photoluminescence signal. (Absorption measurements of our samples were not attempted, since the bandgap of the strained  $\text{Si}_{1-y}\text{C}_y$  alloys was expected to be below that of the silicon substrate.) A different group<sup>17</sup> reportedly confirmed the results of Demkov and Sankey using a photoluminescence study.

Since no information about the band structure of  $\text{Si}_{1-y}\text{C}_y$  alloys had been published by 1994, we decided to pursue the issue of determining the higher (direct) band gap energies of  $\text{Si}_{1-y}\text{C}_y$  alloys. There is a number of modulation spectroscopy techniques available for this task, all with certain advantages and disadvantages.<sup>18</sup> One of these techniques is spectroscopic ellipsometry,<sup>19</sup> which is very useful for rapid, contactless, and non-destructive characterization of semiconductor wafers. This technique has been applied successfully to obtain information about the higher band gaps of  $\text{Si}_{1-x}\text{Ge}_x$  alloys<sup>20</sup> and about the dependence of these gaps for Si under uniaxial stress.<sup>21</sup>

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## EXPERIMENTAL SETUP AND RESULTS

Three  $\text{Si}_{1-y}\text{C}_y$  alloys with thicknesses between 100 and 200 nm and carbon contents of 0.6%, 1.2%, and 1.4% were grown pseudomorphically on Si (001) substrates using molecular beam epitaxy at low temperatures as described elsewhere.<sup>11,13</sup> The samples were characterized and the pseudomorphic growth mode was verified with a variety of techniques as mentioned above.

Using a commercial spectroscopic ellipsometer<sup>22</sup> of rotating-analyzer type, we determined the dielectric functions of these three samples (and that of a device-grade silicon wafer for comparison) between 2.5 and 4.5 eV. The resulting spectra are similar to those of Si<sup>21</sup> and are not shown here. In order to determine the energies of the  $E_1$  and  $E'_0$  critical points (the dominant direct gaps in this spectral range, originating from transitions along the  $\Lambda$ - and  $\Delta$ -directions in the Brillouin zone, respectively), we calculated numerically the second derivatives of the four spectra with respect to energy, see the symbols in Fig. 1. From these spectra, we determined the positions of the  $E'_0$  and  $E_1$  energies as a function of carbon content by comparison with analytical lineshapes<sup>18</sup> (solid lines) normally applied in modulation spectroscopy to such transitions in diamond-type semiconductors.<sup>20,21</sup> The results of this line-shape analysis are shown by the circles in Fig. 2. For clarity, the corresponding energies of the silicon control sample were subtracted. Similar results for the same samples were obtained by Lange *et al.*<sup>23</sup> We also added data from the literature<sup>12</sup> obtained using electroreflectance at 77 K (squares) in Fig. 2.

## COMPARISON WITH CONTINUUM ELASTICITY THEORY

So far, our data tell us nothing about the failure or success of the virtual crystal approximation to describe  $\text{Si}_{1-y}\text{C}_y$  alloys. (Neither does Ref. 12, by the way.) In order to make such a statement, we have to compare our experimentally determined energy dependence on composition with a theoretical model. While a through discussion of this model<sup>24</sup> is beyond the scope of this report, we briefly describe the most important features:

Due to the pseudomorphic growth mode, our samples are biaxially strained. Based on harmonic continuum elasticity theory, this strain is decomposed into a purely hydrostatic expansion and a pure shear strain (uniaxial compression) along the growth direction. The hydrostatic component shifts, but does not split, the electronic transitions. The (001) shear strain splits the  $E_1$  gap, but only one of two transitions is observed in our experimental configuration with polarized light. The  $E'_0$  critical point may also split under this uniaxial stress, but no accurate predictions can be made, since the exact location in the Brillouin zone of the transitions causing this critical point is not known. Experimental evidence<sup>25</sup> indicates that the  $E'_0$  transitions in Si are essentially insensitive to applied (001) stress for our polarization. Based on these symmetry arguments, the expected contributions of hydrostatic pressure and uniaxial stress to the shifts of  $E'_0$  and  $E_1$  with composition can be estimated, if the well-known deformation potentials for Si are used. Finally, we have to consider the alloy shifts for (hypothetical) unstrained or free-standing alloys. For simplicity, we assume that the  $E'_0$  and  $E_1$  energies interpolate linearly between the corresponding gaps in silicon and diamond. The latter assumption is basically given by the virtual crystal approximation (if the quadratic correction terms are neglected). Once all three components are added, we obtain the solid lines in Fig. 2.

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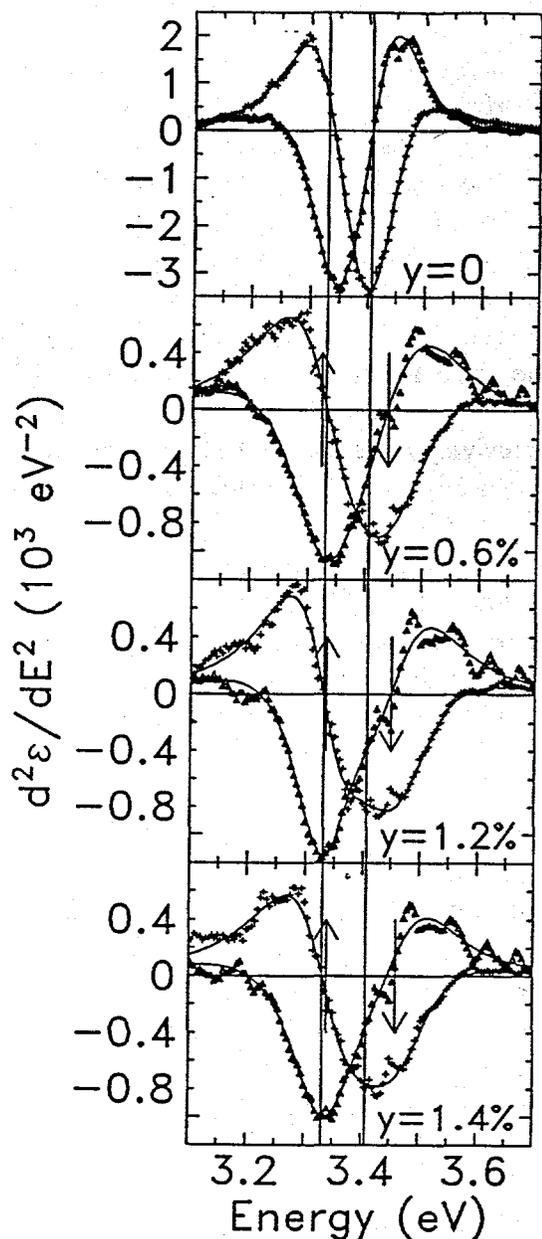


FIG. 1. Numerical derivatives  $d^2\epsilon/dE^2$  of the dielectric function with respect to photon energy (symbols) along with fits to numerical lineshapes (solid lines) for pseudomorphic  $\text{Si}_{1-y}\text{C}_y$  alloys with different carbon content  $y$ . The vertical lines indicate the position of the  $E'_0$  and  $E_1$  critical points in silicon determined from the sample with  $y=0$ . The arrows pointing upward (downward) indicate the positions of the  $E'_0$  and  $E_1$  transitions (for  $y \neq 0$ ) as determined from the line-shape analysis.

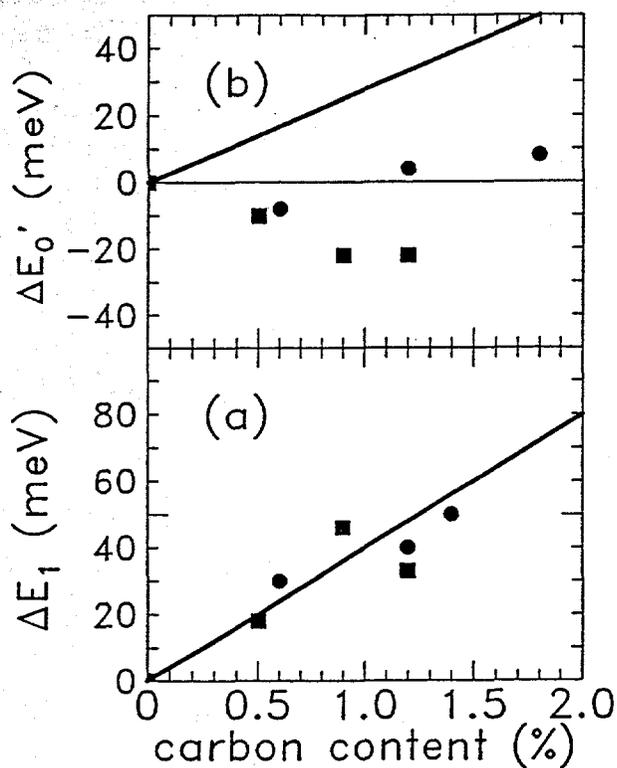


FIG. 2.  $E_1$  (a) and  $E'_0$  (b) critical-point energies from Fig. 1 (squares) and from Ref. 12 ( $\bullet$ ). The corresponding energies of bulk Si have been subtracted for clarity. The straight line shows the expected increase of the energies with increasing carbon content (due to hydrostatic expansion, uniaxial compression along the growth direction, and composition) as described in the text.

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## DISCUSSION AND CONCLUSION

Figure 2 shows excellent agreement of the experimental data obtained by two different groups. This is not surprising, in view of the advanced state and previous successes of modulation spectroscopy<sup>18</sup> in combination with a line-shape analysis. It is striking, however, that  $E_1$  increases with increasing carbon content  $y$ , whereas  $E'_0$  is essentially independent of  $y$  (within the accuracy of the line-shape analysis).

It is also striking that the virtual-crystal approximation for unstrained  $\text{Si}_{1-y}\text{C}_y$  alloys in combination with continuum elasticity theory (using established deformation potentials for Si) to take into account the bixial strain yields perfect agreement with both experimental data sets for  $E_1$ , but not for  $E'_0$ . For completeness, we mention that Kissinger *et al.*<sup>12</sup> observed a decrease of the  $E_2$  critical point with increasing carbon content. Although the response of  $E_2$  to (001) uniaxial stress has not been studied in silicon, it seems that this experimental fact cannot be explained within the virtual crystal approximation for any reasonable value of the  $E_2$  shear deformation potential.

One might speculate about the origins of this discrepancy. Demkov and Sankey<sup>16</sup> predicted that the corrections to the virtual crystal approximation might be  $k$ -dependent, therefore the experimental findings are not unreasonable. We would like to add, however, that the  $E'_0$  transitions are poorly understood in general, even in bulk Si, Ge, or GaAs, since it is very difficult to calculate band gaps and optical properties because of the breakdown of the local-density-approximation.

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## REFERENCES

- <sup>1</sup> J. C. Bean, *Science* **230**, 127 (1985).
- <sup>2</sup> B. S. Meyerson, *Sci. Am.* **270** (3), 62 (1994).
- <sup>3</sup> S. S. Iyer, G. L. Patton, J. M. C. Stork, B. S. Meyerson, and D. L. Harnage, *IEEE Transactions on Electron Devices* **36**, 2043 (1989).
- <sup>4</sup> R. H. Parmenter, *Phys. Rev.* **97**, 587 (1955).
- <sup>5</sup> A.-B. Chen and A. Sher, *Phys. Rev. B* **22**, 3886 (1980).
- <sup>6</sup> S. Zollner, C. H. Grein, and M. Cardona, in *Ultrafast Laser Probe Phenomena in Bulk and Microstructure Semiconductors IV*, edited by R. R. Alfano, *Proc. SPIE* **1677**, 75 (1992).
- <sup>7</sup> M. A. Renucci, J. B. Renucci, and M. Cardona, in *Proceedings of the Second International Conference on Light Scattering in Solids*, edited by M. Balkanski, (Flammarion, Paris, 1971), p. 326.
- <sup>8</sup> J. Weber and M. I. Alonso, *Phys. Rev. B* **40**, 5683 (1989).
- <sup>9</sup> S. de Gironcoli, S. Baroni, and P. Gianozzi, in *20th International Conference on the Physics of Semiconductors*, edited by E. A. Anastassakis and J. D. Joannopoulos, (World Scientific, Singapore, 1990), vol. 2, p. 877.

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- <sup>10</sup> K. Eberl, S. S. Iyer, S. Zollner, J. C. Tsang, and F. K. LeGoues, *Appl. Phys. Lett.* **60**, 3033 (1992).
- <sup>11</sup> S. S. Iyer, K. Eberl, M. S. Goorsky, F. K. LeGoues, J. C. Tsang, and F. Cardone, *Appl. Phys. Lett.* **60**, 356 (1992).
- <sup>12</sup> W. Kissinger, M. Weidner, H. J. Osten, and M. Eichler, *Appl. Phys. Lett.* **65**, 3356 (1994).
- <sup>13</sup> A. R. Powell, K. Eberl, F. K. LeGoues, B. A. Ek, and S. S. Iyer, *J. Vac. Sci. Technol. B* **11**, 1064 (1993).
- <sup>14</sup> J. C. Tsang, K. Eberl, S. Zollner, S. S. Iyer, *Appl. Phys. Lett.* **61**, 961 (1992).
- <sup>15</sup> S. Zollner and R. T. Collins, (unpublished).
- <sup>16</sup> A. A. Demkov and O. F. Sankey, *Phys. Rev. B* **48**, 2207 (1993).
- <sup>17</sup> G. H. Loehelt, M. A. Meléndez-Lira, and J. Menéndez, *Bull. Am. Phys. Soc.* **40**, 220 (1995). (This conference paper was cancelled by the authors.)
- <sup>18</sup> M. Cardona, *Modulation Spectroscopy*, (Academic, New York, 1969).
- <sup>19</sup> R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light*, (North-Holland, Amsterdam, 1977).
- <sup>20</sup> J. Humlíček, M. Garriga, M. I. Alonso, and M. Cardona, *J. Appl. Phys.* **65**, 2827 (1989).
- <sup>21</sup> P. Etchegoin, J. Kircher, and M. Cardona, *Phys. Rev. B* **47**, 10292 (1993).
- <sup>22</sup> J. A. Woollam Co., Inc, 650 J Street, Suite 39, Lincoln, NE 68508.
- <sup>23</sup> R. Lange, S. Zollner, K. G. Jensen, K. M. Myers (unpublished).
- <sup>24</sup> S. Zollner, (unpublished).
- <sup>25</sup> F. H. Pollak and G. W. Rubloff, *Phys. Rev. Lett.* **29**, 789 (1972).

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