DEPOSITION OF MONOLAYER-SCALE GERMANIUM/SILICON HETEROSTRUCTURES BY RAPID THERMAL CHEMICAL VAPOR DEPOSITION

A. ST. AMOUR AND J.C. STURM
Princeton University, Dept. of Electrical Engineering, Princeton, NJ 08544

ABSTRACT

Deposition of monolayer scale Ge/Si heterostructures by Rapid Thermal Chemical Vapor Deposition has been achieved for the first time. All previous work in this area was by Molecular Beam Epitaxy. We have observed the change in Ge growth rate at 500°C as the Si substrate was covered by the first monolayer of Ge. Auger Electron Spectroscopy and Raman scattering experiments determined that the CVD growth mode for Ge on Si (100) at 550°C is Stranski-Krastanov, with the transition to islanding occurring after three monolayers.

INTRODUCTION

Ordered incorporation of Ge in Si has the potential for enhancing the performance of existing heterostructure devices by reducing alloy scattering. Futhermore, certain zone-folded Ge/Si superlattice structures[1] which are predicted to have a quasi-direct band gap offer the possibility of Si based optical devices. All previous experimental work in this area has been by Molecular Beam Epitaxy (MBE).[2]

This paper describes the growth of thin (0.4-13ML) Ge layers on Si (100) by Rapid Thermal Chemical Vapor Deposition (RTCVD). All of the samples used for this work were grown in a RTCVD reactor. In this reactor, four inch substrates are suspended on quartz pins inside a quartz tube. The substrate is heated radiatively from below by a bank of tungsten-halogen lamps, and the wafer temperature is accurately controlled by feeding back the transmission through the wafer of 1.3μm laser light.[3] For all samples, the silicon source was silane and the germanium source was germane; these gases were diluted in hydrogen. The growth pressure was 6 torr, and the growth temperatures were 500°C and 550°C. The hydrogen flow rate was 3slpm, and the germane flow rate was 0.8sccm. Layer thickness and composition were controlled via the reactant flows. That is, during germanium deposition only germane was admitted to the reactor, and during silicon deposition only silane was admitted. Between these steps, neither gas was allowed to flow for a period 30 seconds so that all of the previous gas could be removed before the next was introduced. The resultant structures were characterized by Auger Electron Spectroscopy (AES), Rutherford Backscattering Spectroscopy (RBS), and Raman Scattering Spectroscopy.

The AES experiments were performed in an *in situ* UHV analysis chamber that is connected to our growth reactor via a load lock. Wafers may be transferred from the growth chamber to the analysis chamber immediately after growth and returned to the growth chamber following AES without breaking vacuum. The AES experiments at each temperature were performed in this manner on a single wafer. The primary beam energies used were 1keV and 3keV for Ge layers grown at 500°C and 550°C, respectively. The primary beam current was approximately 10μA in both cases. AES intensities were measured as the peak-to-peak height of the digitally differentiated output of a CMA. Rutherford Backscattering Spectroscopy (RBS) was performed with 2 MeV helium ions and at a backscattering angle of 175°. The samples were rotated to avoid ion channeling. For the normal incidence Raman scattering measurements, 514.5nm radiation from an argon laser was used as the excitation source. The excitation power was 50mW, and the energy resolution of the spectrometer was about 2cm^{-1}.

GROWTH OF GERMANIUM ON SILICON

The initiation of heteroepitaxy of Ge on Si by CVD is very different than that by MBE. Provided that all sticking coefficients are near unity, the growth by MBE of the first monolayer of Ge will proceed at the same rate as the second and all subsequent monolayers. One should expect a much different result for CVD heteroepitaxy. Prior to the initial deposition, the chemical reaction which results in growth takes place between germane and a bare (or hydrogen terminated) silicon surface. After one or more monolayers have been deposited, this reaction takes place between germane and a bare (or hydrogen terminated) germanium surface. One should not expect the growth rate for the first monolayer to equal the average growth rate for thick Ge layers. Similarly, the growth rate for the first monolayer will not be constant. Rather, it will be a function of the Ge coverage of the surface. The growth rate is a function of the Ge coverage of the surface largely because the equilibrium concentration of sites not terminated with hydrogen on a Ge surface is much higher than that on a Si surface. Since only these hydrogen-free sites are active for growth, slower low temperature growth rates result for Si than for Ge.[4]

Figure 1 shows areal density of germanium per layer as a function of growth time for two growth conditions as described above which differed only in temperature. The data for each temperature was acquired by Rutherford Backscattering Spectroscopy from a single sample. The individual germanium layers in each sample were separated by thick silicon spacers so that their RBS spectra could be resolved. The amount of germanium in each layer was determined by integrating the RBS spectrum due to each layer and correcting for its depth from the surface. The change in growth rate with surface coverage is evident at 500°C.

This RBS data is corroborated by Auger Electron Spectroscopy (AES) experiments performed on layers grown at 500°C. The Si substrate AES intensity should decay exponentially as the surface is uniformly covered by Ge. For a constant growth rate and planar deposition, one then should expect the Si intensity to decay exponentially as growth time is increased. In the case of islanding of Ge or intermixing of Ge and Si, the decay of the Si intensity will be more gradual. Plotted in Figure 2 is the Si (LMM) AES intensity for Ge growth times from 10 to 240 seconds. The Si intensity decreased slowly for the first 150 seconds and then dropped more rapidly. This is consistent with the initially slow growth rate seen in Figure 1. The behavior of the Si intensity can also be explained by islanding whereby the substrate intensity is not significantly diminished until the Ge islands grow large and begin to coalesce, but this would be accompanied by a much stronger Ge signal than was observed (see Figure 2 inset).

Assuming that deposition occurs simultaneously on the Ge covered portion of the surface and on the bare silicon portion but at different rates and that Ge atoms initially deposited on existing Ge covered areas quickly diffuse to a bare Si site (this assumption of planar growth is justified later), the growth rate during deposition of the first monolayer of Ge on Si is given by

$$R_1 = (1 - \theta_{Ge}) \cdot R_{Si} + \theta_{Ge} \cdot R_{Ge} \qquad (1)$$

where θ_{Ge} is the fraction of the surface covered with Ge and R_{Si} and R_{Ge} are the growth rates of Ge on Si and of Ge on Ge, respectively. Integrating eq. 1 yields θ_{Ge} for Ge coverages less than one monolayer as a function of time, t.

$$\theta_{Ge}(t) = \frac{R_{Si}}{R_{Ge} - R_{Si}} \left(e^{(R_{Ge} - R_{Si}) \cdot t} - 1 \right) \qquad (2)$$

R_{Ge}, the growth rate of Ge on Ge, is just the slope $\frac{dN_{Ge}}{dt}$ for N_{Ge} greater than one monolayer (0.78×10^{15} cm^{-2}). The activation energy for R_{Ge} was 390meV, agreeing well with that determined from thick Ge layers grown under similar conditions.[4] Keeping only R_{Si} as an adjustable parameter, the RBS data of Figure 1 for 500°C was fit to eq. 2. For this procedure, the intersection of the constant slope and a line at one monolayer was used as an additional data point. At 500°C, the ratio of growth rates $R_{Ge}:R_{Si}$ was 51. These growth rates were indistinguishable at 550°C.

An initially slow growth rate for Ge on SiO$_2$ at 450°C similar to that which we have observed at 500°C on Si has been reported by others.[5] This delay in Ge deposition has been attributed to the reduction of the oxide by germane prior to Ge deposition. These effects are not observed for oxide-free substrates. The wafer cleaning procedure used for this work yielded wafers with oxygen coverage too low to be detected by AES. Such an amount of oxide is far too little to account for the effects we observed.

STRUCTURAL CHARACTERIZATION OF GERMANIUM FILMS

The Si substrate AES intensity can be used to ascertain the growth mode of Ge on Si. Exponential decay of the Si intensity with a decay length of 2.2 monolayers[6] is evidence of planar growth, while slower decay indicates islanding of Ge or intermixing of Ge and Si. Figure 3 shows Si (LMM) intensity for Ge coverages between 0 and 10 monolayers deposited at 550°C. Ge coverages were determined from the growth rate fit to the data of Figure 1. The behavior of the Si intensity following Ge deposition at 550°C is consistent with the Stranski-Krastanov growth mode (initially planar growth followed by islanding), with the transition to islanding occurring at three monolayers. Similar results have been seen in MBE experiments[7], although the presence of hydrogen in CVD may be expected to alter the surface energetics. The persistence of the Si intensity past ten monolayers of Ge coverage can also be explained by intermixing of the Ge layer with the Si substrate by thermal diffusion.

To determine whether the growth after three monolayers was islanding or whether interdiffusion occurred, Raman scattering from Ge/Si superlattices was analyzed. All superlattice structures were grown at 550°C and contained either five or ten periods. These structures were followed by silicon caps grown at 625°C for 10 minutes. The Ge content of each period was determined by dividing the total RBS signal by the number of periods.

Figure 4 provides a comparison of the Raman spectra from three superlattice samples. Sample #1553 consists of ten periods with 2.0 monolayers of Ge per period, sample #1554 consists of ten periods with 4.0 monolayers each, and sample #1577 consists of 5 periods with 13 monolayers each. All three spectra show peaks near 300cm^{-1} and 400cm^{-1} due to the Ge-Ge mode and the Ge-Si mode, respectively.[8]

The peak position and width of the Ge-Ge Raman signal is matrix dependent. This mode appears at 302cm^{-1} in pure Ge crystals, while it is near 285cm^{-1} in low Ge content alloys, depending on composition[9] and strain[10]. Its FWHM for bulk Ge samples is less than 4cm^{-1}, whereas for alloys its width is ~30cm^{-1}. In Figure 5, both the peak position and peak width of the Ge-Ge mode are plotted as a function of the number of Ge monolayers per period. Values for alloy samples are plotted on the vertical axes for reference. Clearly, as Ge content per period was increased, the Ge-Ge mode behaved in a more bulk-like fashion. This is a strong indication that the thicker layers were not intermixed by diffusion. Also, the peak position of the Ge-Ge mode increased rapidly between two and six monolayers, indicating the appearance of large, relaxed Ge clusters. Compressive strain in an alloy also shifts the Ge-Ge mode to higher energies, but this would not be accompanied by a decreased line width. Thus, we conclude that the Ge deposited on Si at 550°C is planar up to three monolayers and islanded for addition deposition.

SUMMARY

We report the first monolayer scale deposition of Ge/Si heterostructures by Rapid Thermal Chemical Vapor Deposition. We have grown Ge layers with coverages of 0.4 to 13 monolayers on Si (100) and have observed by AES and RBS the change in growth rate at 500°C as the initially bare Si surface is covered with Ge. By AES and Raman scattering, we have determined that the growth mode for Ge on Si (100) at 550°C is Stranski-Krastanov with islanding after three monolayers.

REFERENCES

1. U. Gnutzmann and K. Clausecker, Appl. Phys. 3, 9 (1974).
2. H. Presting et al, Semicond. Sci. Technol. 7, 1127 (1992).
3. J.C. Sturm, P.V. Schartz, and E.J. Prinz, J. Vac. Sci. and Tech. B9, 2011 (1991).
4. P.M. Garone et al, Appl. Phys. Lett. 56 (13), 1275 (1990).
5. Ishwara Bhat and Wen-Sheng Wang, Appl. Phys. Lett. 64 (5), 566 (1994).
6. H.-J. Gossmann, L.C. Felman and W.M. Gibson, Surf. Sci. 155, 413 (1985).
7. H.-J. Gossmann and G.J. Fisanick, Surf. Sci. Lett. 244, L117 (1991).
8. D.W. Feldman, M. Ashkin and James H. Parker, Jr., Phys. Rev. Lett. 17 (24), 1209 (1966).
9. M.A. Renucci, J.B. Renucci and M. Cardona, Light Scattering in Solids (Flammarion, Paris, 1971), p. 326.
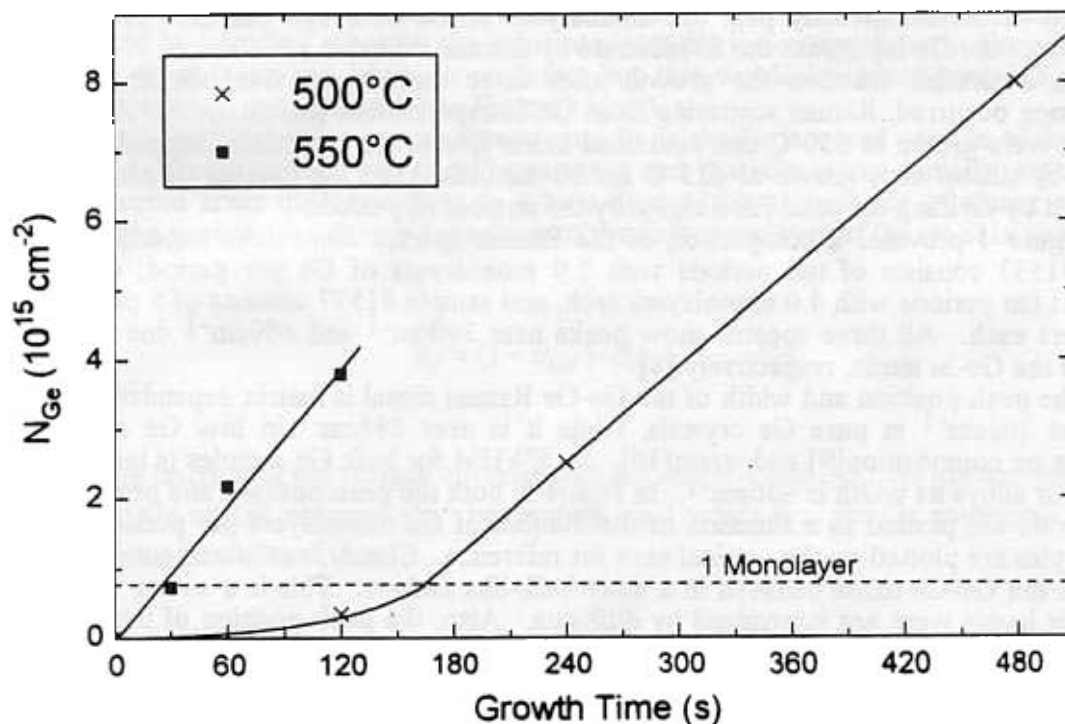10. F. Cerdeira et al, Appl. Phys. Lett. 45 (10), 1138 (1884).

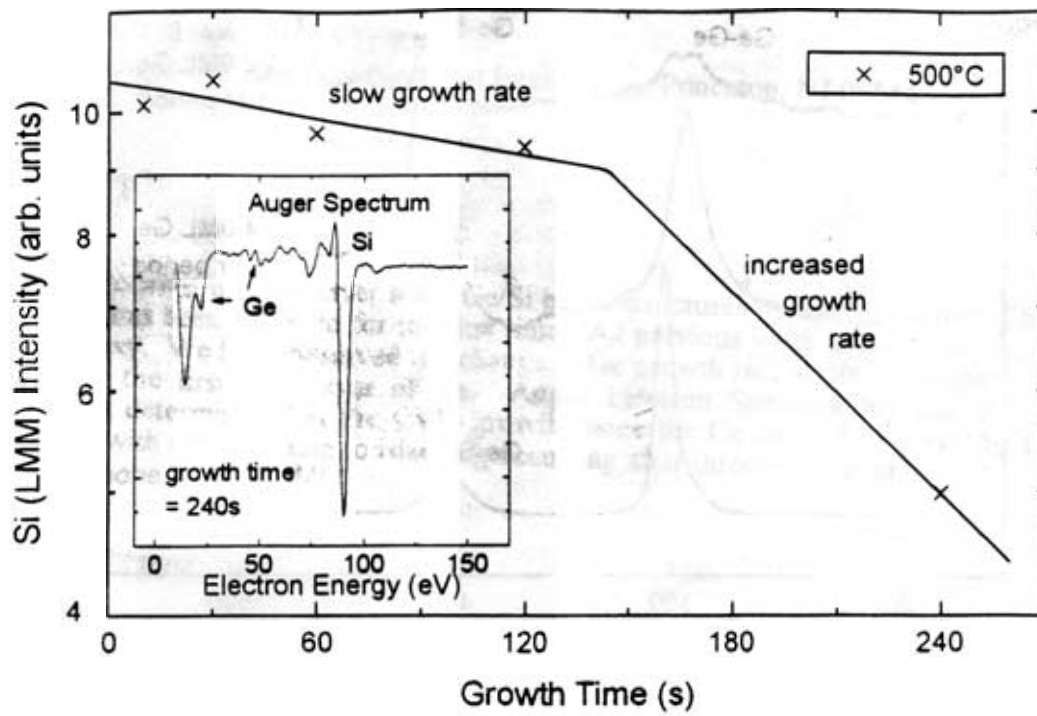Figure 1. Ge coverage on Si as a function of growth time at 500°C and 550°C

Figure 2. Si substrate AES intensity as a function of Ge growth time at 500°C. Inset shows an AES spectrum for a Ge growth time of 240s.
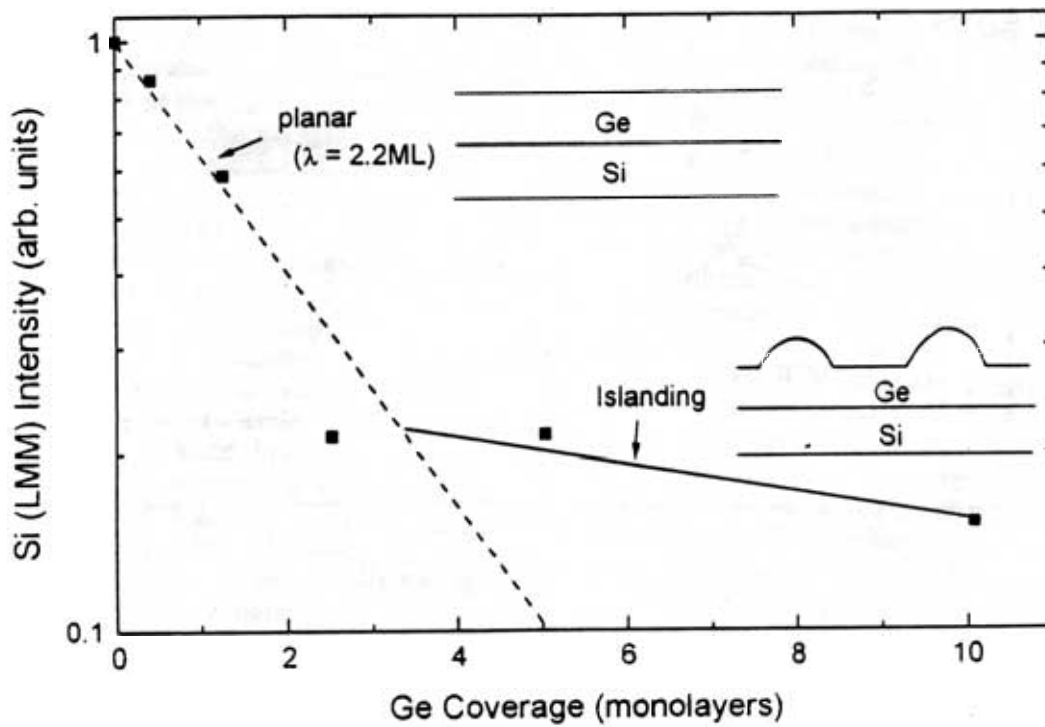

Figure 3 Si substrate AES intensity as a function of Ge coverage for growth at 550°C
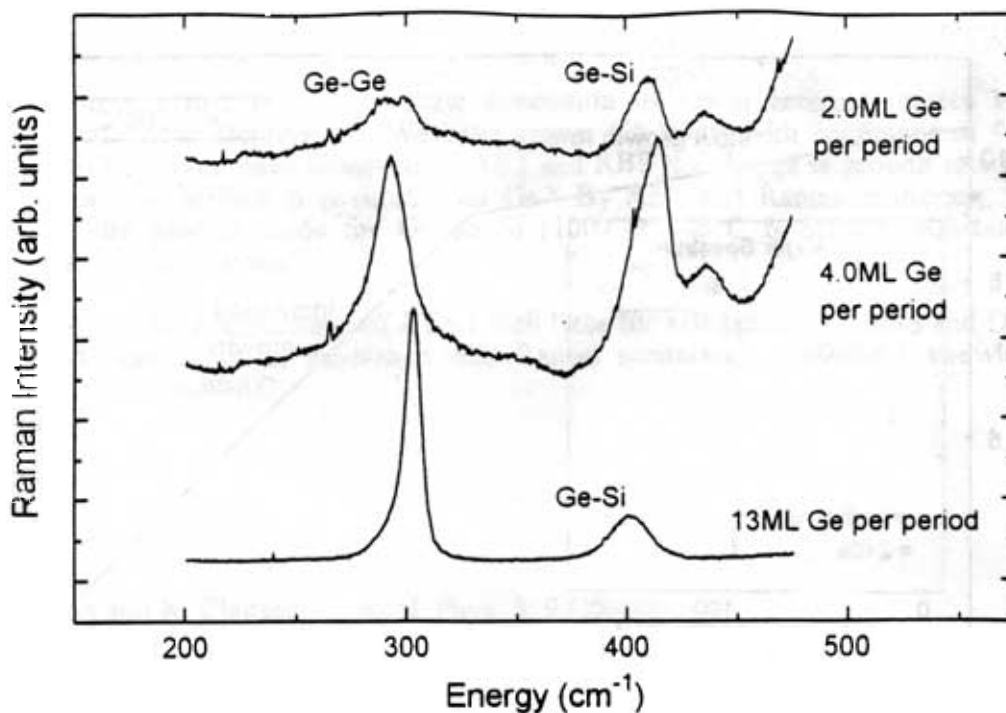
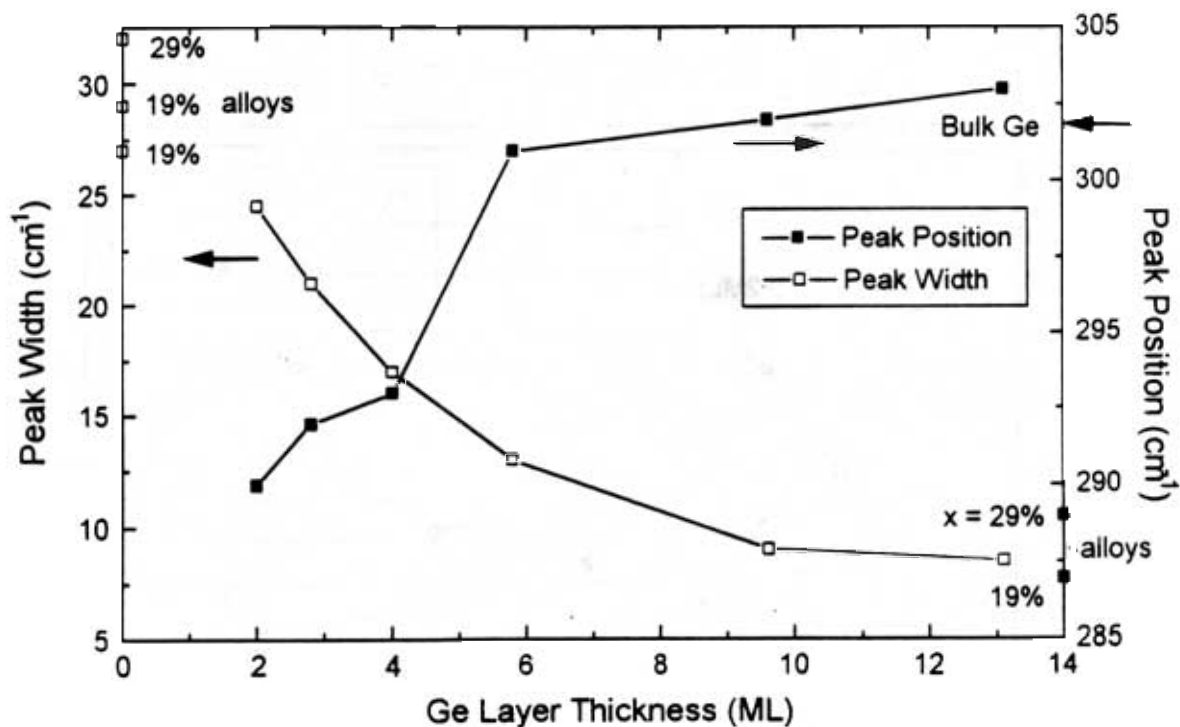Figure 4. Raman scattering spectra of Ge/Si superlattices.

Figure 5. Peak position and peak width of the Ge-Ge Raman mode as a function of Ge monolayers per superlattice period. Values for some $Si_{1-x}Ge_x$ alloys and for bulk Ge are provided for reference.