# RAMAN STUDY OF THE ANNEALING-INDUCED STRUCTURAL EVOLUTION OF AN a-Si:H/a-Ge:H SUPERLATTICE

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# RAMAN STUDY OF THE ANNEALING-INDUCED STRUCTURAL EVOLUTION OF AN a-Si:H/a-Ge:H SUPERLATTICE

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**Raman scattering was used to follow the structural and layer-composition changes which accompany annealing of an a-Si:H/a-Ge:H superlattice. Following significant intermixing in the amorphous phase, two separate crystallization events are resolved: sudden crystallization of the Ge-rich layers followed by gradual crystallization of the Si-rich layers. Ultimately, compositional homogenization occurs.**

## 1. Introduction

This paper presents a Raman-scattering study of the structural changes accompanying annealing in an a-Si:H/a-Ge:H superlattice. While the structural evolution in this system is complex, Raman scattering is effective for distinguishing among the various phases.[1,2,3] Recent Raman work on crystalline $Si_{1-x}Ge_x$ alloys[4,5] allows this technique to be used to determine composition (x) in the crystallized layers, and recent diffusion studies[6] of amorphous Si/Ge multilayers are also available for comparison to our Raman results.

## 2. Experiment

The investigated superlattice was prepared by PECVD techniques described elsewhere.[7] The intended structure consisted of thirty cycles of a-Si:H (sublayer thickness $d_{Si}$=30 nm) alternating with a-Ge:H (sublayer thickness $d_{Ge}$=5.5 nm). The top layer was a-Si:H, with the bottom a-Ge:H sublayer on a 69 nm a-Si:H buffer layer deposited on a c-Si substrate. The deposition plasma was halted between layers to achieve abrupt interfaces. Rutherford backscattering confirmed the superlattice structure. Furnace anneals were done in air for 20-minute periods.

Raman measurements were carried out in a back-scattering configuration[8] using the 1.916 eV red line of a Kr laser. For back scattering, $1/(2\alpha)$ is a conservative measure of the optical penetration depth $d_{opt}$. At 1.916 eV, $d_{opt}$ values estimated from the relevant

absorption coefficients $\alpha$ yield $(d_{opt}/d_{Si})$=15 for a-Si:H and 50 for c-Si, $(d_{opt}/d_{Ge})$=4 for a-Ge:H and 7 for c-Ge. Thus several near-surface cycles (to a depth of about 150 nm) are probed in these experiments, the thinner but more absorptive Ge layers being the limiting factor.[9] Laser power was kept below 10 mW, and a spectral slit width of 4 $cm^{-1}$ was used. Long scanning times (15 to 90 hours) were needed to yield clean spectra.

## 3. Results: Amorphous Interdiffusion and Two Crystallizations

Figure 1 presents our results. The annealing sequence begins with the as-grown a-Si:H/a-Ge:H multilayer and ends with a homogeneous crystalline alloy. Table 1 lists the peak positions and observed linewidths (full width at half maximum) estimated by deconvoluting these spectra.

A 400 C anneal (not shown), like the unannealed sample, revealed only the two broad bands corresponding to the dominant bands of a-Ge:H (272 $cm^{-1}$) and a-Si:H (477 $cm^{-1}$). But at 525 C, a third broad band appears which corresponds to a-$Si_{1-x}Ge_x$:H alloys.[1] Using the x=0.45 Raman spectrum reported in Ref. 1, the relative Si-Ge and Ge-Ge intensities observed for the 525 C anneal,[10] and a simple model assuming a-Si:H/a-$Si_{0.5}Ge_{0.5}$:H/a-Ge:H in place of a graded interface, we estimate that the alloyed regions contain 30% of the Ge atoms. This corresponds to an interface-alloy thickness of 1.6 nm. This can be compared to the equivalent diffusion-determined thickness given by $L^2=(16/\pi)Dt$, using $D=1.0\times10^{-3}$ $(nm)^2s^{-1}$ extrapolated from Ref. 6. This calculation yields L=2.5 nm, in quite reasonable agreement with our Raman-derived experimental result.

The 600 C anneal is noteworthy because the Ge-rich layers have crystallized while the Si-rich layers remain predominantly amorphous. A weak c-Si peak is, however, already present, superimposed on the a-Si band, as seen in Fig. 1 and listed in Table 1. Table 1 includes composition estimates for the crystalline phases, obtained from:

$$\bar{\nu}(\text{Si-Si}) = 521-62x-11x^2 \quad , \quad x = 0.016\Delta-0.000034\Delta^2 \quad , \quad (1)$$

$$\bar{\nu}(\text{Ge-Ge}) = 301-31y+17y^2 \quad , \quad y = 0.025\delta+0.0018\delta^2 \quad , \quad (2)$$

where x is the Ge fraction, y=1−x is the Si fraction, $\bar{\nu}$ is in $cm^{-1}$, $\Delta=521-\bar{\nu}(\text{Si-Si})$, and $\delta=301-\bar{\nu}(\text{Ge-Ge})$. These relations are our fits to the c-$Si_yGe_x$ room-temperature data of Refs. 4 and 5; they provide a convenient method for estimating x and y. The estimate based on (1) is the more reliable one, since $\bar{\nu}$(Si-Si) shifts quickly and nearly linearly

Table 1. Raman peak positions and linewidths, in $cm^{-1}$, and layer-composition estimates.

| Anneal Temp. | Si-Si band $\bar{\nu}$ | Si-Si band FWHM | Si-Ge band $\bar{\nu}$ | Si-Ge band FWHM | Ge-Ge band $\bar{\nu}$ | Ge-Ge band FWHM | x of "Si layer" | y of "Ge layer" |
|---|---|---|---|---|---|---|---|---|
| as-grown | 477 | 65 | — | — | 272 | 46 | 0 | 0 |
| 525 C | 477 | 79 | 376 | 66 | 270 | 47 | | |
| 600 C | 475 | 76 | | | | | | |
| | 517 | 15 | 399 | 26 | 296 | 15 | 0.06 | 0.2 |
| 650 C | 518 | 13 | 399 | 28 | 296 | 14 | 0.05 | 0.2 |
| 725 C | 517 | 15 | 403 | 30 | 294 | 15 | 0.06 | 0.3 |
| 810 C | 503 | 11 | 405 | 24 | 288 | 18 | 0.28 | 0.6 |
| 900 C | 502 | 8 | 403 | 23 | 284 | 15 | 0.29 | 0.9 |

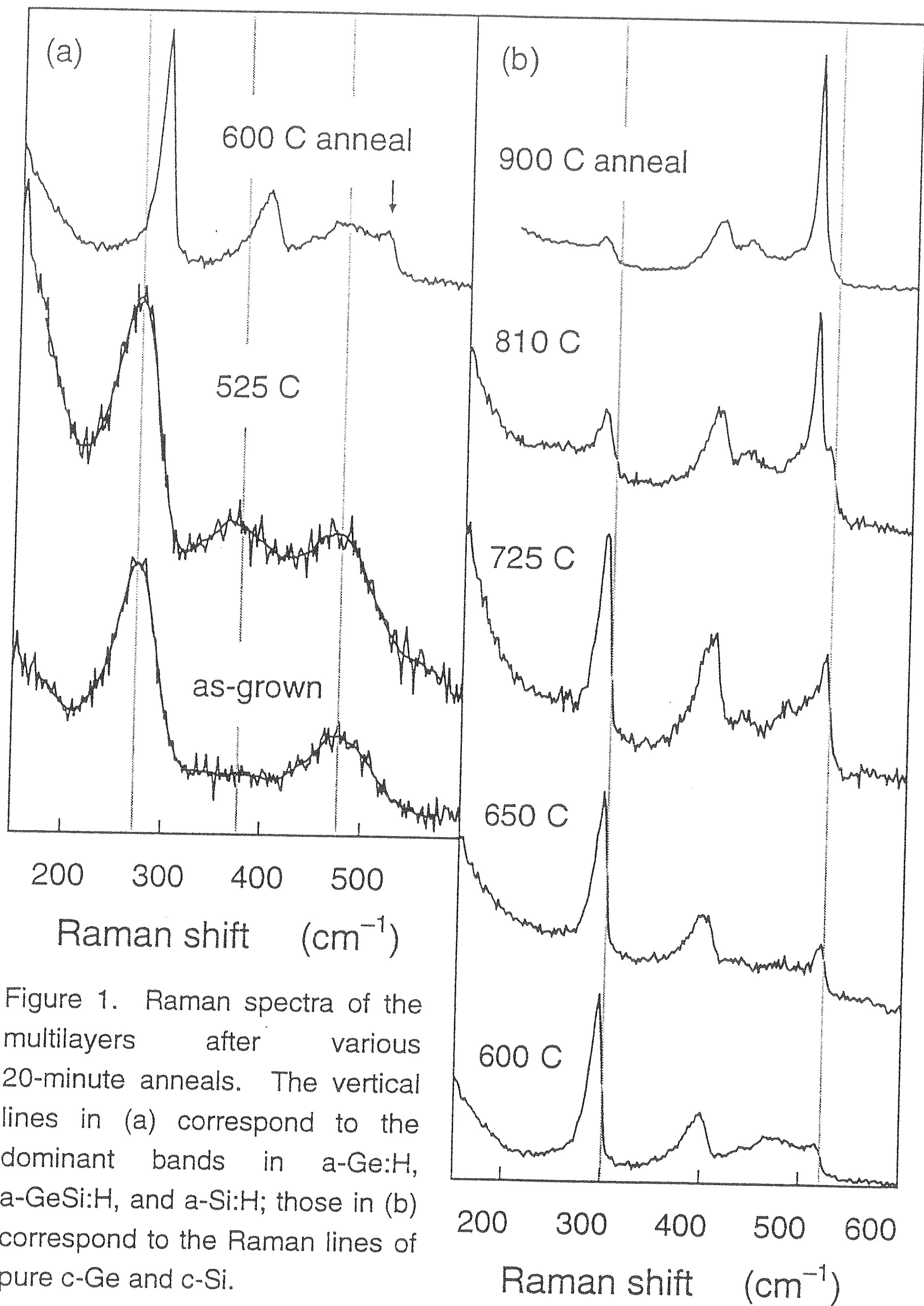


Figure 1. Raman spectra of the multilayers after various 20-minute anneals. The vertical lines in (a) correspond to the dominant bands in a-Ge:H, a-GeSi:H, and a-Si:H; those in (b) correspond to the Raman lines of pure c-Ge and c-Si.

with x. The crystalline alloys also display[4,5] a composition-insensitive narrow band near 400 $cm^{-1}$; this Si-Ge band is present in our spectra for 600 C and above.

The position and sharpness of the Ge-Ge and Si-Ge lines seen for the 600 C anneal show that the Ge-rich layers are crystalline, and $\bar{\nu}$(Ge-Ge) indicates, via (2), that the composition is about $Si_{0.2}Ge_{0.8}$. Note that we can be confident, from (1), that the weak sharp line at 517 $cm^{-1}$ does not arise from Si-Si vibrations in the x=0.8 Ge-rich layers, but instead arises from a small crystalline component in the Si-rich layers. This is confirmed by the growth of this line at higher anneals of 650 C and 725 C. The composition of these layers, from $\bar{\nu}$(Si-Si) and (1), is about $Si_{0.94}Ge_{0.06}$.

Figure 1 and Table 1 show that at 650 C and 725 C, the crystallization of the Si-rich layers proceeds while the layer compositions change little. At 810 C and 900 C, the shifted sharp lines signal composition changes, and Table 1 indicates that x+y is now roughly unity (the y estimate is uncertain for large y). We interpret these results to represent the homogenization of the multilayer. In fact, our 900 C anneal spectrum is essentially identical to that reported, in Fig. 1(b) of Ref. 4, for c-$Si_{0.72}Ge_{0.28}$. This composition is Ge-rich relative to that corresponding to complete intermixing of the original superlattice ($Si_{0.86}Ge_{0.14}$); we attribute this to rejection of Ge from the silicon oxide surface layer expected for this high-temperature anneal.

## 4. Summary

The spectral signatures documented in Fig. 1 and Table 1 clearly demonstrate the compositional and structural changes which occur as a result of annealing-induced diffusion and crystallization. The intermediate structure arrived at in the 600 C anneal was close to a crystal/glass superlattice with alternating Ge-rich crystalline and Si-rich amorphous layers.

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10. We assume the scattering efficiency of a-$Si_{0.5}Ge_{0.5}$:H to be half that of a-Ge:H, and correct for the difference between measured spectra (our Fig. 1) and reduced Raman (Ref. 1).

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