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THE PROPERTIES OF Si/$Si_{1-x}Ge_x$ FILMS GROWN ON Si SUBSTRATES BY CHEMICAL VAPOR DEPOSITION*

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A growth parameter study was made to determine the properties of a SiGe superlattice-type configuration grown on Si substrates by chemical vapor deposition (CVD). The study included such variables as growth temperature, layer composition, layer thickness, total film thickness, doping concentrations, and film orientation. Si and SiGe layers were grown using SiH_4 as the Si source and GeH_4 as the Ge source. When intentional doping was desired, diluted diborane for p-type films and phosphine for n-type films were used. The study led to films grown at ~1000°C with mobilities from ~20 to 40 percent higher than that of epitaxial Si layers and ~100 percent higher than that of epitaxial SiGe layers grown on (100) Si in the same deposition system for net carrier concentrations of $\sim 8x10^{15} cm^{-3}$ to $\sim 2x10^{17} cm^{-3}$. Enhanced mobilities were found in multilayer (100)-oriented Si/$Si_{1-x}Ge_x$ films for layer thicknesses ≥ 400Å, for film thicknesses $>2\mu m$, and for layers with $x = 0.15$. No enhanced mobility was found for (111)-oriented films and for B-doped multilayered (100)-oriented films.

Key words: epitaxy, chemical vapor deposition, SiGe alloys, superlattice, enhanced mobility.

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Introduction

Over the past few years there have been several reports of enhanced electron mobility in multilayer superlattice (1, 2) and single-layer GaAs-GaAlAs (3-6) heterostructures grown both by molecular beam epitaxy (MBE) and metalorganic-chemical vapor deposition (MOCVD). It was considered of interest to determine if multilayered superlattice-type Si/SiGe structures grown on Si substrates would also show enhanced electron mobility. If so, one might be able to make use of the vast wealth of Si technology that is available today. Unfortunately, the almost perfect lattice match between GaAs and GaAlAs does not occur in the Si/SiGe system, and the type of defects observed by Kasper and co-workers (7) in their examination of a SiGe superlattice grown by UHV epitaxy were expected to provide mobilities lower than bulk Si. As shown in this paper, mobilities lower than bulk Si are, in fact, measured in single layers of SiGe grown on Si substrates; but we found that multilayer Si/SiGe films on (100) Si can possess enhanced mobility (8).

We chose to study the growth of the multilayer structure by chemical vapor deposition (CVD) using the hydrides as the sources of Si and Ge. CVD growth of SiGe alloys on Si using the halides was reported as early as 1962 by Oda (9) and Miller and Grieco (10) and in 1972 by Aharoni and co-workers (11), but films from the halides require high growth temperatures (~1100-1200°C) (11, 12) and layer and dopant interdiffusion would be expected at these temperatures. In addition, the generated HCl would also be expected to offer problems in composition and doping control of very thin layers due to a competing film-growth and etch-back process. On the other hand, epitaxial SiGe layers have been grown from the hydrides on Ge as low as 800°C (13) and on Si as low as 1000°C (14). We prepared Si and SiGe alloy layers and films from one SiH_4 source (5% in He) and two GeH_4 sources (~5.5% in H_2 and in He) in a Pd-purified H_2 carrier gas on high resistivity single crystal p-type Si substrates. Intentionally added dopant species were from proportioned flows of phosphine (PH_3, 45ppm in He) and diborane (B_2H_6, 46ppm in He). Total gas flows were about 3 lpm.

Experimental

Apparatus

The films were grown in a CVD reactor system, a schematic of which is shown in Figure 1. It consists essentially of (a) a reactant gas manifold and distribution line system of mostly ¼-inch (0.64 cm) valving, filters, and flow controls; (b) a vacuum pumping system for evacuating selected portions of the reactor system as needed; (c) provisions for burning the reactor system exhaust gases; (d) a 75mm diameter vertical quartz deposition chamber with provision for supporting the substrates normal to gas flow on a rotatable SiC-coated radio-frequency heated graphite susceptor. An automatic sequence timer with a mechanical counter in series is used to control solenoid-activated air-operated valves for rapid and precise flow control of the gases and reactants. Doping gases were injected into the SiH_4 line. A separate line was used for the GeH_4, with both lines joining near the top of the deposition chamber. Temperatures were measured with an optical pyrometer that was focused on the side of the rf-heated susceptor. The actual temperature at the top of the susceptor is lower than the reported as-measured temperature by about 50^oC when the side-temperature is about 1000^oC.

Measurement Techniques

Various analytical methods were used to measure the properties of the grown films. The Van der Pauw (15) method was used to determine resistivity and Hall coefficient, from which carrier concentration and carrier mobility were calculated; scanning electron microscopy (SEM) and Auger techniques were used to measure layer and film thicknesses; X-ray diffraction and Auger analysis were utilized to determine crystalline quality and alloy composition of the $Si_{1-x}Ge_x$ films.

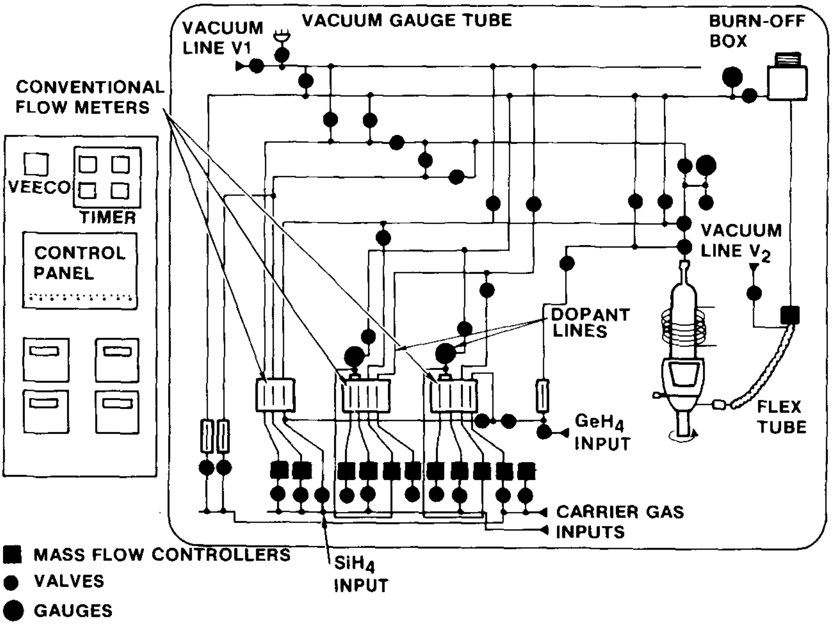

Fig. 1. Schematic Diagram of Si CVD Reactor System.

Results and Conclusions

Growth Temperature Studies

The initial phase of the experiments determined the minimum temperature at which reasonable quality single-layer films of Si and SiGe could be grown in our system on (100)-oriented Si substrates. The temperature range 900-1000°C was examined; and based on the reflectivity and smoothness of these (100)-oriented films, 1000°C was established as a preferred growth temperature. As shown in Figure 2, during these early experiments it was found that the incorporation of Ge into the film was temperature dependent, i.e., more Ge in the film at 900°C than at 1000°C for the same reactant gas flow rates. The wall deposit was heavy when SiH_4-GeH_4 mixtures were pyrolyzed, and the growth rate was mainly influenced by the SiH_4 flow at a

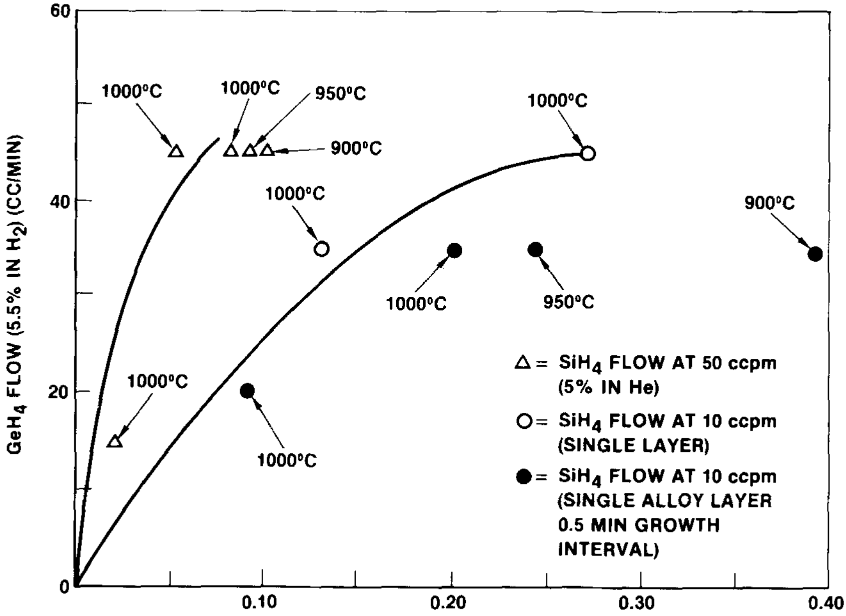

Fig. 2. Effect of GeH$_4$ Flow and Growth Temperature on Film Composition of Si$_{1-x}$Ge$_x$ Alloy Layer

growth temperature of ~1000°C. Si films were high resistivity, and SiGe films were n-type (~10^{16} cm^{-3}) at growth rates of ~0.3μm/min. At this growth rate and temperature the Ge mole fraction was ~0.08-0.10. By lowering the SiH$_4$ flow (from a value of 50 to 10ccpm), the films became p-type for rates of ~0.1μm/min. using the original tanks of SiH$_4$ and GeH$_4$. The films became more p-type as the Ge content increased (up to at least 0.27 mole fraction Ge), thereby necessitating the addition of an n-type dopant, namely phosphorus, to produce n-type films.

A different tank of GeH$_4$ (~5 percent in He) in combination with the same tank of SiH$_4$ produced n-type SiGe films without intentional doping. It was also determined that single films of Si were n-type with n ~1-2x10^{15}cm^{-3} rather than high resistivity, as previously found. A series of multilayer growth experiments which repeated many of those performed with the first GeH$_4$ tank, but without PH$_3$ additions, led to similar electrical results.

Table I. Characteristics of Si:P, SiGe:P, and Si:P/SiGe:P Films Annealed for 0.5 Min. Between Layers

SEQ. NO.	GROWTH TEMP (°C)	FLOWS (ccpm)* SiH_4-GeH_4	GROWTH TIME (MIN)	TOTAL NO. OF LAYERS	APPROX. THICKNESS		M.F. Ge (EDAX)	RESIST (ohm-cm)	ELECTRON CONC. (cm^{-3})	ROOM TEMP. MOBILITY (cm^2/V-Sec)
					µm	A/LAYER				
15	~1000	50-0	25	1	8	–	–	0.23	3.5×10^{16}	784
16	~1000	50-45	25	1	9	–	0.08	0.52	1.9×10^{16}	620
17	~1000	50-0 50-45	0.2 0.2	20	1.2	600		1.1	1.7×10^{16}	347
23	~950	50-0	50	1	9	–	–	0.47	2.3×10^{16}	569
24	~950	50-45	25	1	10	–	0.09	0.27	5.2×10^{16}	442
20	~950	50-0 50-45	0.2 0.2	100	5.2	520		0.43	1.1×10^{16}	1330
11	~900	50-45	25	1	10	–	~0.10	0.17	1.3×10^{17}	276(p-type)
21	~900	50-0 50-45	0.4 0.2	100	6.6	660		0.26	1.6×10^{16}	1469
39	~900	50-0 50-45	0.1 0.1	100	3.2	320		0.52	8.8×10^{15}	1370

Table I compares the properties of phosphorus-doped single and multiple layered Si and SiGe films and multilayered Si/SiGe films grown at the higher rate at the three different temperatures. We note that the thicker, ~10 mole percent Ge films grown even as low as 900°C show comparatively high mobilities (~1350cm^2/V-sec for n ~$10^{16}cm^{-3}$) even though the films can be expected to be compensated. During the early stages of growth the films were gray, but they slowly changed in reflectivity as they became thicker, ending as semi-reflective films. The thickness of each Si and SiGe layer was controlled by injecting the reactants into the deposition chamber for a specified time period. In the study 0.5 min was arbitrarily used between layer growths to purge the lines and reactor of residual dopants and reactants. Thus, the 100-layer structure shown in Figure 3 was produced at ~950°C by 0.2 min bursts of the silane source at 50ccpm and 0.2 min bursts of the combined SiH_4 and GeH_4 sources, the latter at 45ccpm. Rutherford Backscattering (RBS) analysis and Auger composition profiles of such structures made at an etch rate of ~700Å/min by Ar ion bombardment suggested that Si, SiGe interfaces were not completely abrupt, as shown in Figure 4 for a typical Auger scan representing just a few layers of a film grown early in the program. The shape of the curve suggests there may be a 100-200Å transition layer between the

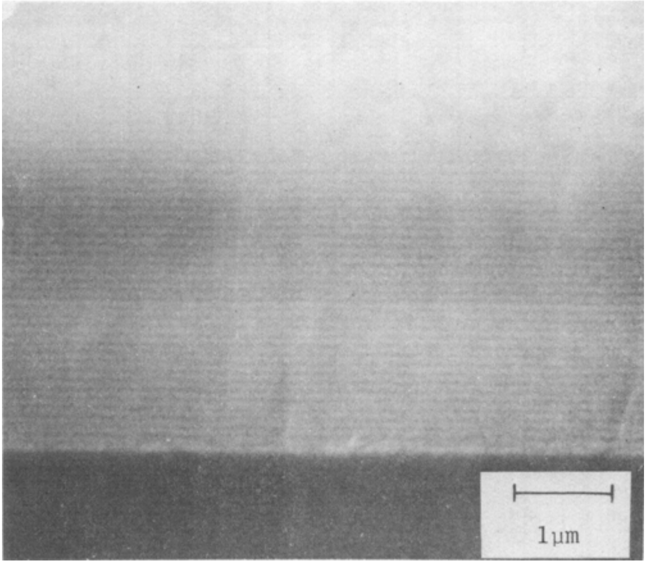

Fig. 3. SEM Photograph of an Alternating, Multilayer Si/Si$_{0.85}$Ge$_{0.15}$ Film, ~5µm Thick. The individual Si and SiGe layers are ~500Å thick, as determined by an Auger Profile.

Si and SiGe alloy layers, caused perhaps by elemental diffusion between layers or by residuals in the deposition system that are not completely removed after layer deposition and become subsequently incorporated into the next growing layer.

Layer Thickness Dependence

The room temperature mobilities of thick multilayer Si/SiGe films grown at ~1000°C at the lower growth rate (~0.1µm/min) using both GeH$_4$ cylinders for Si$_{1-x}$Ge$_x$ layer compositions of $x = 0.10$ and $x = 0.15$ are shown in Figure 5 as a function of the Si layer thickness. In all cases, the thickness of the SiGe layer was either equal to or greater than that of the Si layer. The doping levels in the SiGe films are ~10^{16}cm^{-3}; in the Si, ~10^{15}-10^{16}cm^{-3}. The data indicate higher mobilities in the layered Si/SiGe films

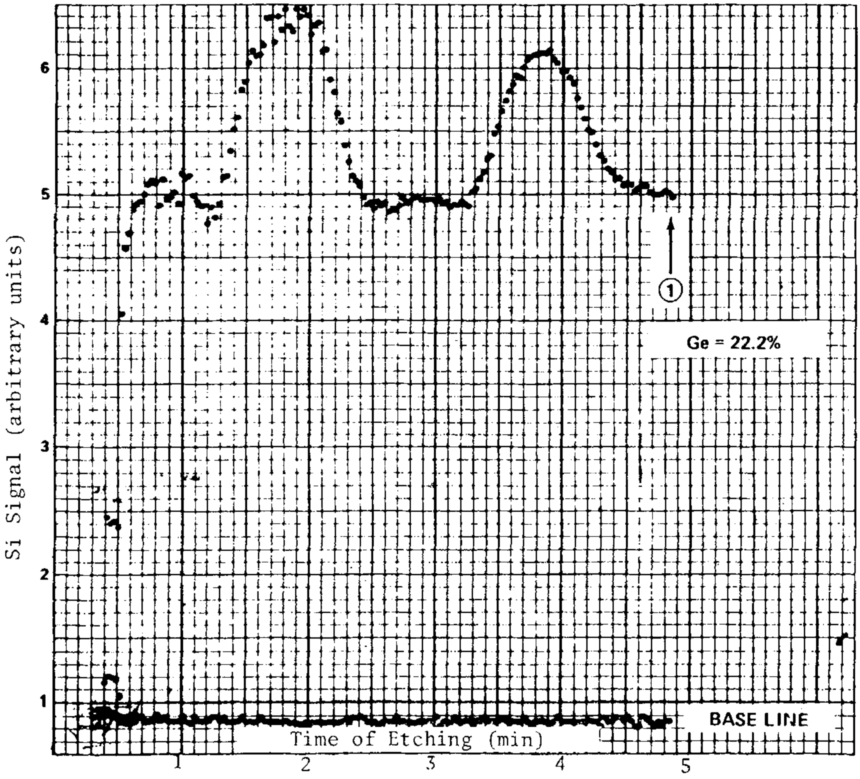

Figure 4. Auger Profile of the Si Content in Several Layers of an Alternating, Multilayer Film with X=0.22. The Ge content was determined by direct measurement of the Ge signal at several selected points.

with ~15 mole percent Ge in the SiGe layers for a Si layer thickness of ≥400Å. Good mobilities (~1000 cm^2/V-sec) were found for multilayer films with Si layer thicknesses as thin as 250Å.

In this figure, in the sequences 29, 53, and 54, the Si layer thickness was kept constant at ~400Å and the SiGe layer thickness was progressively increased from ~400Å to ~1500Å. The results (a <10 percent mobility difference) indicate the thickness of the SiGe layer has little effect on the electrical properties of film grown under these conditions of temperature, growth rate, layer composition, etc.

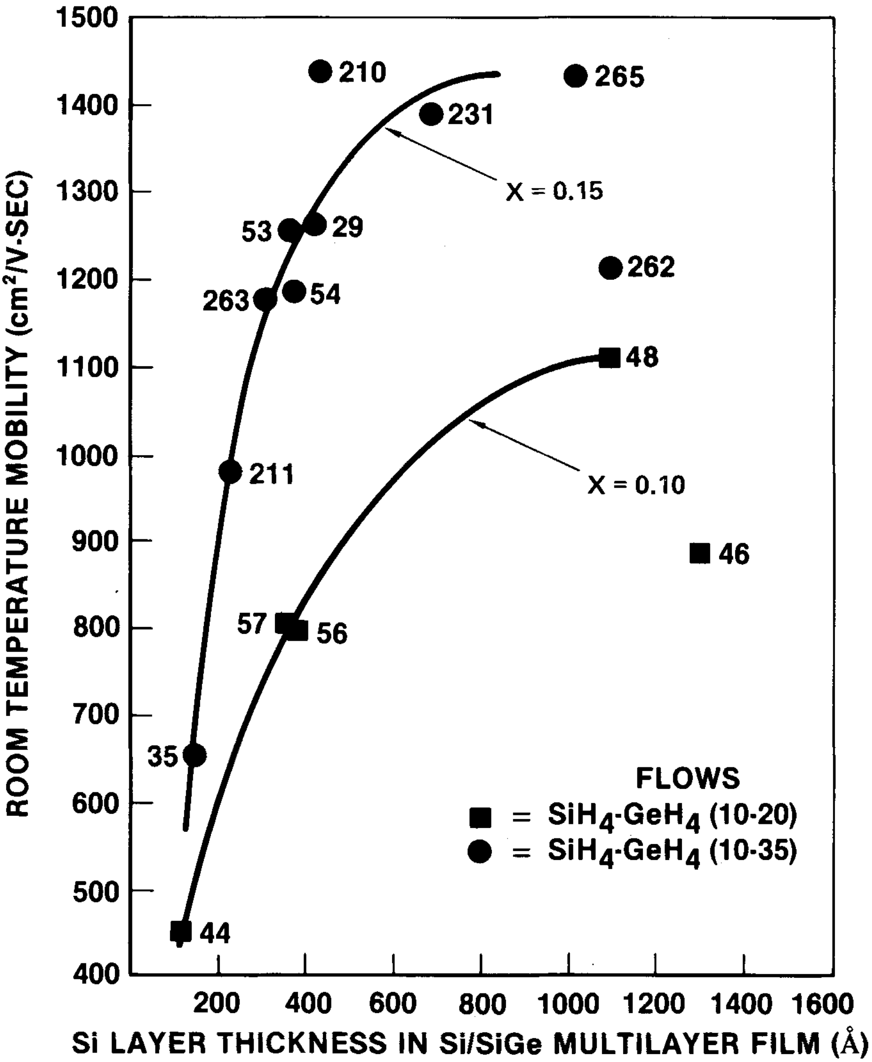

Fig. 5. Mobility Versus Si Layer Thickness in Si/Si$_{1-x}$Ge$_x$ Multilayer Films with $x=0.10$ and $x=0.15$. Layer growth rates were ~0.1μm/min at a growth temperature of ~1000°C; measured carrier concentrations were from 8×10^{15}-3×10^{16} cm^{-3}.

Film Thickness Dependence

The electrical properties of the alternating Si/SiGe multilayer films were found to be dependent on the total film thickness for films $\leq 2\mu m$ thick. The results shown in Figure 6 include data for two different sets of films: one in which the Si layers are about 500Å thick; the SiGe layers, ~1000Å thick; the other, for films grown with layers of different thickness produced using the same injection times for the Si and SiGe layer in each film (from 0.3 min to 1.5 min). We have produced high quality films with mobilities as high as ~1750 cm^2/V-sec at room temperature and ~10,000 cm^2/V-sec at 77K.

Comparatively poor electrical results were obtained for layers grown for an injection time of 0.2 min for silane flows of 10ccpm. This may be due to a combination of insufficient gas mixing in the reactor and layer interdiffusion, for even the SEM at high magnification was unable to reveal a layered pattern in such films.

Orientation Effects

Table II provides a comparison between the electrical properties of several "undoped" 0.25, 2.0 and 4.5µm single SiGe and multilayer alternating Si/SiGe films grown under similar conditions at ~1000°C on (100) Si and (111) Si substrates. The (100)-oriented Si/SiGe multilayer film exhibits higher electron mobility than its (111) counterpart at

Table II. Effect of Substrate Orientation on Film Properties (Growth Temp ~1000°C)

SEQ. NO.	SUBSTRATE ORIENT.	FLOWS (ccpm) $SiH_4 \cdot GeH_4$	GROWTH TIME (MIN)	TOTAL NO. OF LAYERS	APPROX. THICK (µm)	RESIST. (ohm-cm)	CARRIER CONC. (cm^{-3})	MOBILITY (cm^2/V·Sec)
115	100 111	10·35	2.3	1	0.25	0.30 0.50	8.3×10^{16} 3.3×10^{16}	252 376
114	100 111	10·35	20	1	2	1.0 0.6	1.5×10^{16} 2.4×10^{16}	406 474
269	100	10·0 10·35	0.6 0.6	61	4.5	0.36 0.08	1.5×10^{16} 7.9×10^{15}	1165 9462
	111	10·0 10·35	0.6 0.6	61	4.5	0.86 0.33	1.0×10^{16} 5.6×10^{15}	719 3357

room temperature and 77K. This limited data also suggested the single layer (111) SiGe film has slightly higher mobility than the (100) film.

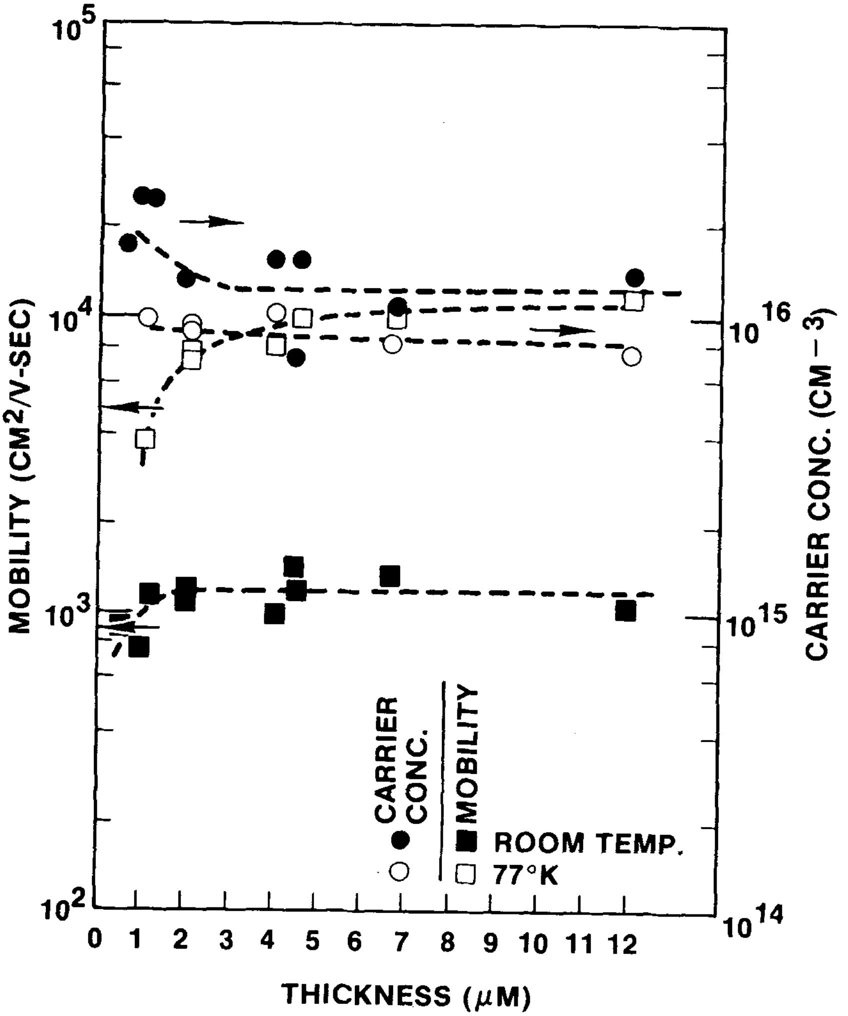

Fig. 6. Carrier Concentration and Mobility Versus Thickness for Undoped Multilayer Si/SiGe Alloys

Carrier Concentration Dependence

To determine the properties of films of Si, SiGe, and multilayered Si/SiGe (100)-oriented films of different electron concentration levels, a PH_3-in-He source was proportioned and mixed with the SiH_4 and SiH_4-GeH_4 mixtures just prior to film growth. The electrical results are summarized in Figure 7 along with data from many other films grown during the course of the study.

The results show a mobility enhancement of from ~20 to at least 40 percent in the multilayer Si/SiGe films over that of epitaxial Si layers and ~100 percent over that of epitaxial SiGe layers for n from $\sim 8\times10^{15}$ to $\sim 10^{17}cm^{-3}$.

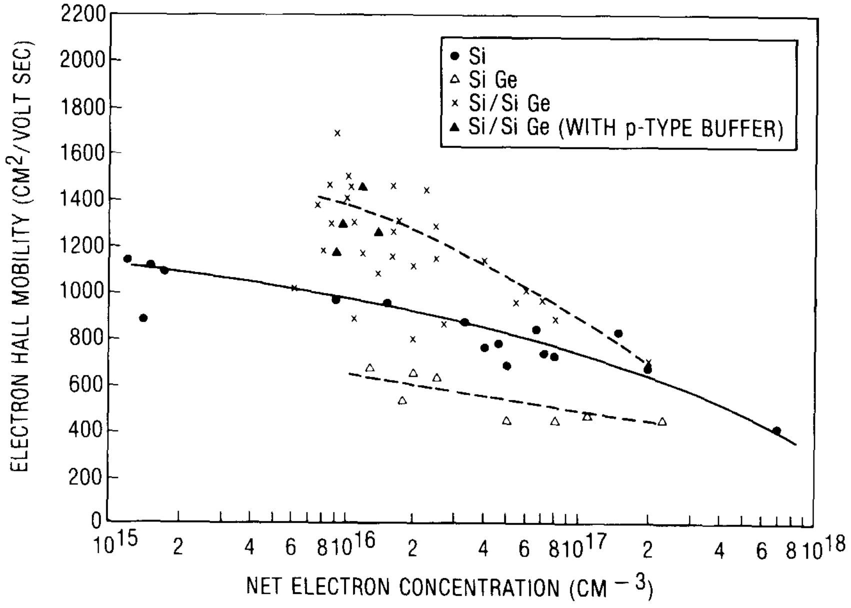

Fig. 7. Electron Hall Mobility vs Net Carrier Concentration for (100)-Oriented Si (•), $Si_{1-x}Ge_x$ (Δ), and Alternating Layer Si/SiGe (x, ▲) Films Grown Under Somewhat Similar Conditions for x Between 0.10 and 0.22 for Film Thickness Between 2.0 and 6.5µm, and Si/SiGe Layer Thicknesses Between 300Å and 1500Å.

The cause of the observed electron mobility enhancement is not obvious. It may be due to stress-induced phenomena (16, 17) caused by the relatively large lattice and thermal mismatch between the layers. The reason for the enhanced mobilities is being studied, and the properties of MESFET's produced from Si and layered Si/SiGe films are being compared. These results will be reported elsewhere.

Limited studies gave no indication that hole mobilities are enhanced in Si:B/SiGe:B multilayers. On the other hand, low mobility values may be due to the fact that the B-doped p-type films are compensated by the n-type impurities present in the "undoped" source gases.

In summary, enhanced mobilities have been measured in multilayer n-type $Si/Si_{1-x}Ge_x$ films with x = 0.15 grown by CVD of the hydrides at ~1000°C on p^-(100)-oriented Si substrates. The mobilities are on the average from ~20 to 40 percent higher than that of homoepitaxial (100) Si layers over the carrier range ~$8\times10^{15}cm^{-3}$ to ~$2\times10^{17}cm^{-3}$ and on the average about 100 percent greater than that of epitaxial SiGe layers grown on (100) Si. Simultaneous growth of Si/SiGe multilayer films on (111)- and (100)-oriented Si substrates produced improved films only on (100) Si. $Si/Si_{1-x}Ge_x$ multilayer films with x = 0.15 and a Si layer thickness ~400Å are electrically superior to films with x = 0.10. The mobilities in Si/SiGe films show dependence on the layer thickness below about 400Å although excellent mobilities (~1000 cm^2/V-sec) have been measured in multilayer films with Si layers only 250Å thick. Limited studies gave no indication that hole mobilities are enhanced in Si:B/SiGe:B multilayer films.

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