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Polycrystalline Ge_xSi_{1-x} thin film formation by chemical vapor deposition using silicon difluoride and germanium tetrachloride as precursors

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Ge_xSi_{1-x} thin films ($x = 0.03$–0.75) were grown on Si(111), quartz and graphite by LPCVD using SiF_2 and $GeCl_4$ as the precursors at 450–700 °C. Thin films prepared at 550–700 °C contained polycrystalline Ge_xSi_{1-x}. The composition of the thin film can be controlled by adjusting the reaction temperature and the relative inlet quantity of $GeCl_4$. A linear correlation between the lattice parameters of the prepared Ge_xSi_{1-x} thin films and the Ge contents x is established. A plausible reaction mechanism is proposed and discussed.

Investigations in recent years have thoroughly elucidated the feasibility of using group IV-based heterojunction bipolar transistors (HBTs) to overcome some of the limitations of silicon homojunction bipolar transistors.[1] Owing to their desirable characteristics of materials compatibility and favorable band gap offsets, Si/Ge_xSi_{1-x} HBTs have been extensively studied.[2] On the other hand, heavily doped p-type poly-Ge_xSi_{1-x} is highly promising as a gate electrode material in submicrometer complementary metal oxide semiconductor (CMOS) technologies, owing to its lower resistivity and variable work function. Silicon germanium alloy films are also of particular interest for fabricating solar cells with high conversion efficiencies.

Previously, Ge_xSi_{1-x} has been deposited by molecular beam epitaxy and by chemical vapor deposition.[3,4] In chemical vapor deposition, GeH_4 and SiH_4 were used as precursors in most reactions.[4] In this study, SiF_2 and $GeCl_4$ are used as the precursors. A somewhat lower deposition temperature may be expected.[5]

Experimental

The Ge_xSi_{1-x} thin films were grown in a hot wall LPCVD reactor. Fig. 1 schematically depicts the experimental setup. The reactor consists of a 30 mm diameter removable quartz tube connected to a SiF_2 generation chamber. The SiF_2 was generated by the reaction of SiF_4 and Si at 1150 °C.[6] $GeCl_4$ (Strem) was used as received. Substrates were Si(111), graphite and quartz. Thin films grown on graphite substrates were used to measure the composition. The substrates were cleaned by conventional procedures to remove grease and then the oxide was etched off just before loading. Substrate temperature was measured with a K-type TC gauge. The general procedure for a deposition run initially involved evacuating the system to a pressure of 10^{-2} Pa. The reactor and the SiF_2 generation chamber were then heated to the desired temperatures. With the system evacuated to 10^{-3} Pa, the SiF_4 gas and the vapor of $GeCl_4$ at room temperature were introduced into the SiF_2 generation chamber and the deposition chamber, respectively. The deposition temperatures were controlled at 450–700 °C. The deposition period was 2 hours. Thin films were occasionally annealed at 800 °C under an argon atmosphere. The volatile products were characterized by FTIR, GCMS and NMR spectroscopy. Compositions of the samples were analyzed by EDS both as-deposited and after annealing. Several samples were also analyzed by X-ray photoelectron spectra.

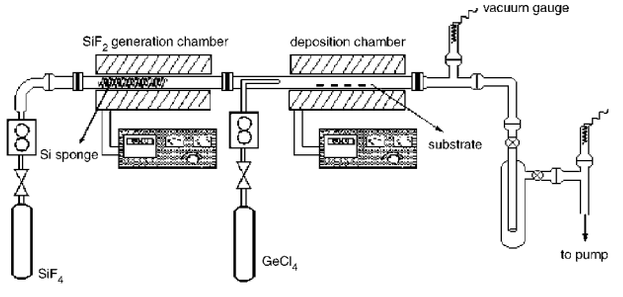

Fig. 1 Schematic diagram of the LPCVD hot-wall reactor with the SiF_2 generator.

SEM was performed in a JEOL 840A microscope, with energy dispersion X-ray analytical capability. X-Ray diffraction (XRD) patterns of the thin films were taken with Cu-Kα radiation using a Siemens D5000 diffractometer. X-Ray photoelectron spectra (XPS or ESCA) were measured on a Physical Electronics PHI 1600 ESCA spectrometer. The NMR spectra were obtained using a Bruker AM 400 spectrometer operating at 376.5 MHz for ^{19}F spectra. Raman spectra were recorded on a Spex 1403 spectrometer, using 488.0 mm Ar^+ laser excitation. GCMS data were obtained by a Shimadzu QP1000 spectrometer. Finally, infrared spectra were obtained on a Perkin-Elmer PC2000 IR spectrometer.

Results and discussion

Ge_xSi_{1-x} thin films of a wide range of compositions ($x = 0.03$–0.75) were deposited on Si substrates in the temperature range of 450–700 °C. The films deposited below 500 °C were amorphous. At temperatures between 550 and 700 °C, polycrystalline thin films were obtained as identified by XRD. The germanium content in those thin films increased with increasing reaction temperature. At a fixed temperature (600 °C), the Ge content in the film increased linearly with the relative inlet

Table 1 Thin film compositions, microstructures and growth rates for different reaction conditions

Deposition temperature/°C	Inlet quantity of SiF_4/sccm	Inlet quantity of $GeCl_4$/sccm	Growth rate/μm h^{-1}	Composition		Microstructure
				%Si	%Ge	
450	4	2	<0.1	97	3	Amorphous
500	4	2	0.9	93	7	Amorphous
550	4	2	1.8	84	16	Polycrystalline
600	4	2	4.3	63	37	Polycrystalline
650	4	2	3.9	51	49	Polycrystalline
700	4	2	<0.1	28	72	Polycrystalline
750	4	2	<0.1	Not detectable		Not detectable
450	3	2	0.4	96	4	Amorphous
500	3	2	0.5	89	11	Amorphous
550	3	2	2.6	75	25	Polycrystalline
600	3	2	3.6	54	46	Polycrystalline
650	3	2	2.9	31	69	Polycrystalline
700	3	2	<0.1	25	75	Polycrystalline
750	3	2	<0.1	Not detectable		Not detectable
600	3	1	2.0	72	28	Polycrystalline
600	6	2	5.4	72	28	Polycrystalline
600	9	3	5.6	69	31	Polycrystalline
600	2	2	2.7	46	54	Polycrystalline
600	3	2	3.6	54	46	Polycrystalline
600	4	2	4.3	63	37	Polycrystalline
600	5	2	4.8	67	33	Polycrystalline
600	6	2	5.4	72	28	Polycrystalline
600	7	2	5.7	80	20	Polycrystalline
600	8	2	5.9	80	20	Polycrystalline
600	3	1	2.0	72	28	Polycrystalline
600	3	2	3.6	54	46	Polycrystalline
600	3	3	2.6	48	52	Polycrystalline
600	3	4	1.2	36	64	Polycrystalline
600	3	5	<0.1	Not detectable		Not detectable

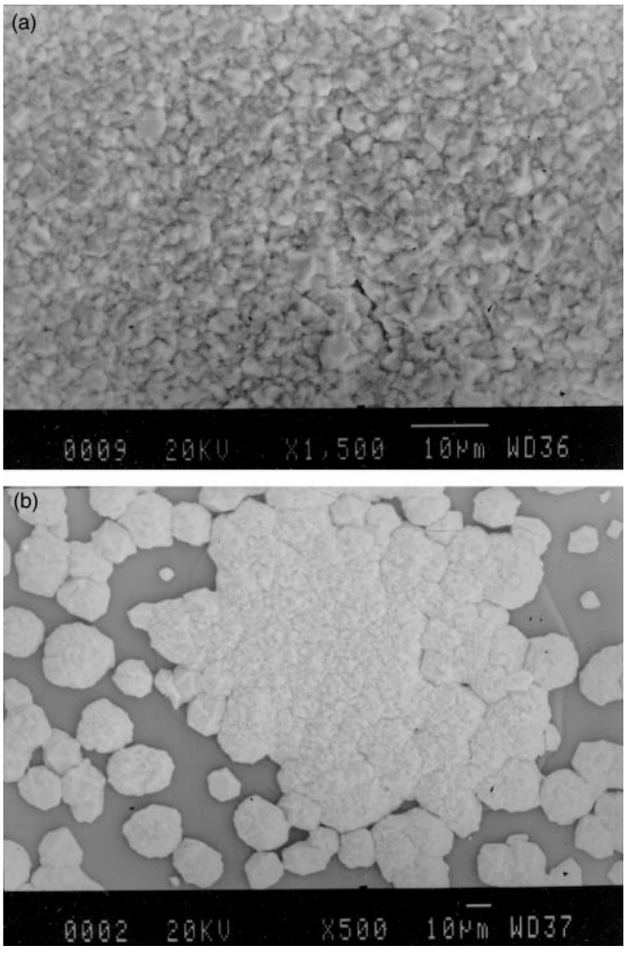

Fig. 2 Surface morphology of thin films grown on a silicon wafer over different deposition periods: (a) deposition time of 1 h and (b) deposition time of 30 min.

quantity of $GeCl_4$. However, the growth rate of the film began to drop as the flow of $GeCl_4$ exceeded that of SiF_4. This can be seen in the last three rows in Table 1. It seems that the back diffusion of $GeCl_4$ into the SiF_2 generation region would cause either a decrease in the SiF_2 yield or react with SiF_2. The real situation is not clear at all at this moment. Table 1 lists the reaction conditions, growth rates, compositions and microstructures of the thin films.

It is known that the disproportionation reaction of SiF_2 proceeds in the temperature range 400–800 °C.[7] The reaction is kinetically favored but thermodynamically disfavored as the reaction temperature increases. >From our previous studies, it occurs that the optimal reaction temperature seems to be 650 °C. Above 700 °C, the reaction slows down, and finally the reverse reaction begins to take over as the temperature is raised above 950 °C.

These observations seem to agree with the data described in Table 1, if the CVD reaction proceeded simultaneously *via* the

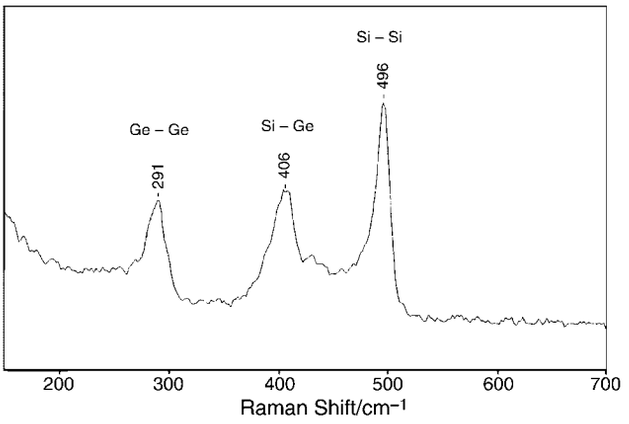

Fig. 3 Raman spectrum of thin film deposited on a silicon substrate at 550 °C.

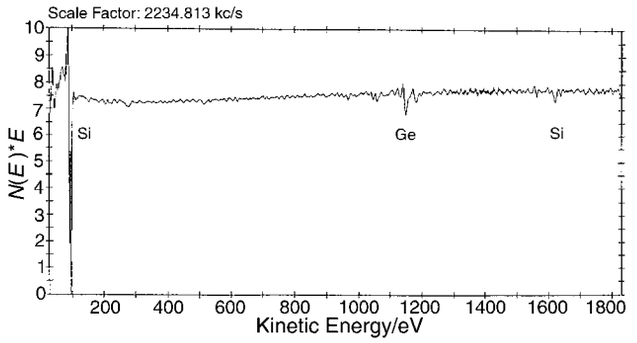

Fig. 4 Auger survey of a thin film grown on a silicon substrate at 550 °C after Ar^+ sputtering.

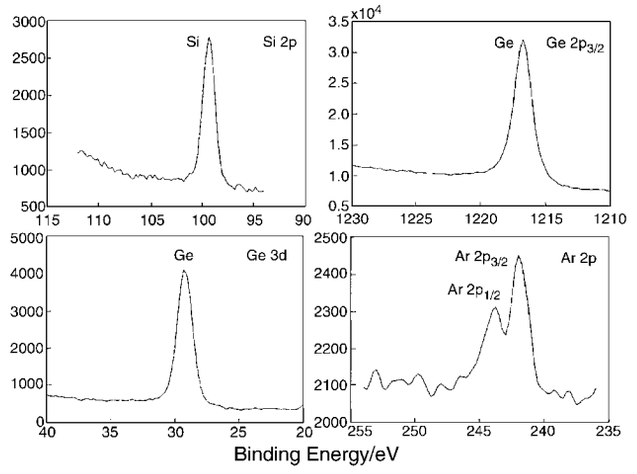

Fig. 5 Typical Ge ($2p_{3/2}$), Ge (3d), Si (2p) and standard Ar (2p) binding energy spectra for the thin film deposited at 550 °C after Ar^+ sputtering.

direct disproportionation of SiF_2 and a Ge-deposition process caused by the chlorine abstraction by SiF_2.

It is interesting to note that at fixed temperature changing the total input of reactants does not seem to affect the relative compositions of Si and Ge in the film, provided the relative inlets of SiF_4 and $GeCl_4$ are kept constant. For example, at 600 °C and a 3 : 1 ratio of SiF_4 : $GeCl_4$ inlets, the film composition remained about 70 : 30 for Si/Ge after an increase of the total input by three times (from 4 to 12 sccm). Beyond 12 sccm total input, the yield of SiF_2 begins to fall because the total pressure in the reaction chamber gets too high, therefore, the film growth rate stops increasing.

Fig. 2 illustrates typical SEM pictures of the Ge_xSi_{1-x} thin film at different deposition times (30 min and 1 h). The characteristic feature of the coating is highly faceted and has

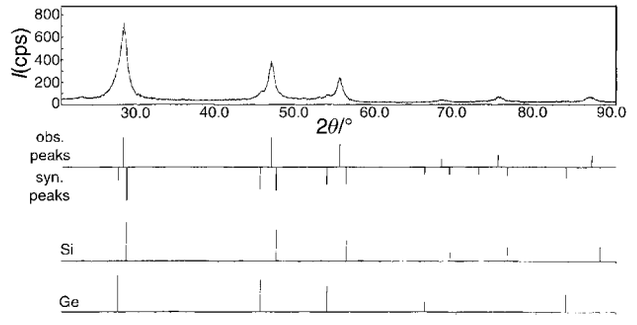

Fig. 6 The X-ray diffraction patterns of $Si_{1-x}Ge_x$ thin film grown on silicon wafer at 550 °C and the combined peaks of silicon and germanium.

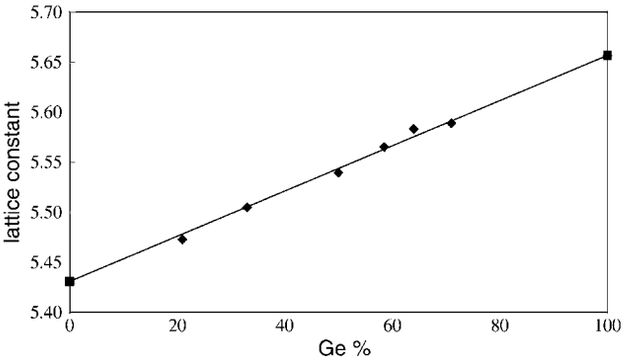

Fig. 7 The relationship of lattice parameter to the content of germanium.

a pyramidal shape. Fig. 2 reveals that the grain sizes on the surface cover a range from 1 to 20 μm.

Fig. 3 illustrates the Raman spectrum of as-deposited Ge_xSi_{1-x} films at 550 °C. The spectrum shows three sharp peaks located at 291, 406 and 496 cm^{-1}, which are assigned to Ge–Ge, Si–Ge and Si–Si vibrations, respectively. These peaks correlate with those of bulk crystalline Ge_xSi_{1-x} alloys.[8]

Fig. 4 is the XPS survey spectrum of a thin film deposited from $GeCl_4$ and SiF_2 at 700 °C, which contains peaks assigned to Si and Ge.

After Ar^+ sputtering for 3 min to remove the surface layer, binding energies of Si(2p) at 99.0, Ge(3d) at 29.0 and Ge($2p_{3/2}$) at 1217.0 eV assigned to Ge_xSi_{1-x} were observed (Fig. 5).

X-Ray diffraction was used for phase identification of the Ge_xSi_{1-x} thin films. Fig. 6 shows an XRD pattern taken from the as-deposited Ge_xSi_{1-x} film. It contained diffraction peaks at 2θ angles 28, 46, 55, 67, 74 and 86°, which are assigned to (111), (220), (311), (400), (331) and (422) diffractions, respectively.[9] Compared with the standard peaks of pure Si and Ge, it is obvious that each of these observed peaks is located in between the corresponding peaks of Si and Ge. This observation reveals a diamond cubic structure similar to that of pure silicon or germanium.

The lattice parameters of Ge_xSi_{1-x} thin films of various compositions were found to have the values between those of pure silicon ($a = 5.431$) and pure germanium ($a = 5.657$ Å).[9] Fig. 7 plots the lattice parameter as a function of the germanium content in the Ge_xSi_{1-x} film; a nice linear relationship is observed.

Fig. 8 depicts the electron diffraction ring pattern of the Ge_xSi_{1-x} thin film. The radius ratio of the circles equals 1 : 1.63 : 1.91. This ratio is comparable to that of a diamond cubic structure, revealing that $r\{111\} : r\{220\} : r\{311\} = 3^{1/2}$:

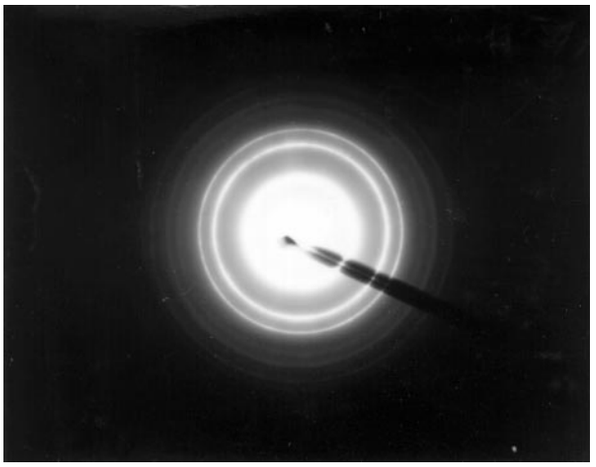

Fig. 8 Electron diffraction pattern of the thin film.

$8^{1/2}:11^{1/2}=1:1.62:1.90$. These results indicate that the Ge_xSi_{1-x} thin film is polycrystalline with a diamond cubic structure[10] in agreement with the XRD study.

During the deposition reactions, the volatile products collected and characterized by FTIR, GCMS and NMR analyses were found to be SiF_4, SiF_3Cl, SiF_2Cl_2, $SiFCl_3$ and $GeCl_4$.

As mentioned earlier, the thin film compositions were proportional to the inlet ratio of SiF_4 and $GeCl_4$, a result indicating that the growth of Si and Ge proceeded independently, and the alloy was formed by annealing. Under our experimental conditions, Si was deposited by the disproportionation reaction of SiF_2; however, $GeCl_4$ did not decompose to form elemental germanium at our reaction temperatures. It is quite obvious that elemental Ge was produced by abstraction of the chlorine atoms in $GeCl_4$ by SiF_2. A plausible reaction mechanism can be proposed to account for all the products observed in the reaction:

$$2SiF_2 \rightarrow SiF_4 + Si$$

$$SiF_2 + GeCl_4 \rightarrow Ge + SiF_{4-n}Cl_n \ (n=1\text{–}3)$$

$$Ge + Si \overset{\text{annealing}}{\rightarrow} Ge_xSi_{1-x}$$

Thus the dual role of SiF_2 both as a silicon source for the thin film produced as well as a scavenger of F and Cl, is evident in this reaction. At lower temperatures the disproportionation of SiF_2 is the dominating reaction, whilst at higher temperatures the chlorine abstraction (to form Ge) becomes the major reaction.

In conclusion, this study demonstrates a convenient process for the generation of Ge_xSi_{1-x} thin films of various compositions ($x=0.03$–0.75), which can be well controlled by adjusting the reaction temperature or the relative inlet quantity of $GeCl_4$. Besides, the linear correlation between the lattice parameters of Ge_xSi_{1-x} films and the Ge contents x makes possible the determination of the film composition by a simple measurement of the lattice parameter.

Acknowledgements

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References

1 N. Kistler and J. Woo, *Int. Electron Devices Meet., Tech. Dig.*, 1993, 727.
2 T. J. King, J. R. Pfiester and K. C. Saraswat, *IEEE Electron Device Lett.*, 1991, 533.
3 C. J. Tsai, P. Rozenak, H. A. Atwater and T. V. Vreeland, *J. Cryst. Growth*, 1991, **111**, 931.
4 T. J. King and K. C. Saraswat, *J. Electrochem. Soc.*, 1994, **141**, 2235.
5 (*a*) C. Y. Lee, J. L. Huang and C. S. Liu, *J. Mater. Chem.*, 1996, **6**, 1131; (*b*) C. C. Cheng, J. L. Yu, C. Y. Lee, C. S. Liu and H. T. Chiu, *J. Mater. Chem.*, 1992, **2**, 983; (*c*) C. Y. Lee and W. C. Yang, *J. Mater. Chem.*, 1999, **9**, 2445.
6 P. L. Timms, R. A. Kent, T. C. Ehlert and J. L. Margrave, *J. Am. Chem. Soc.*, 1965, **87**, 2824.
7 M. Janai, S. Aftergood, R. B. Weil and B. Pratt, *J. Electrochem. Soc.*, 1981, **128**, 2660.
8 (*a*) S. Kodato, *J. Non-Cryst. Solids*, 1985, **77–78**, 893; (*b*) S. M. Prokes and A. K. Rai, *J. Vac. Sci. Technol.*, 1994, **A12**, 1148.
9 Powder Diffraction File, JCPDS International Center for Diffraction Data, 1982, File No. 27-1402 for silicon and 04-0545 for germanium.
10 I. M. Watt, *The principles and practice of electron microscopy*, Cambridge University Press, Cambridge, 1985.