Rapid alloying of silicon with germanium in microwave field using single mode cavity

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Silicon and germanium alloys have been formed for the first time by heating powdered mixtures of 75%Si and 25%Ge in just 2 min in the H field in a single mode 2·45 GHz microwave cavity. As is well known, alloy formation in conventionally heated silicon–germanium mixtures is difficult, even when processed for much longer time durations at the same temperature. Further, any oxide contaminants, if present in the starting material or formed during heating, somehow, appear on the surface of the specimen after microwave treatment.

Keywords: Si–Ge alloy, Microwave, Magnetic field effect

Introduction

The tremendous growth in the application of wireless communication has pushed the demand for high speed circuitry. At present, III–V compound semiconductors are the major players in this field. The cost of production of reliable III–V based devices, however, prohibits their use in large volume consumer electronics. Silicon–germanium alloys may offer an alternative to compound semiconductors. The biggest advantage of silicon–germanium alloys over its rivals lies in its compatibility with complementary metal-oxide semiconductor (CMOS) technology. Further, silicon–germanium alloys have ultrahigh frequency capability and therefore can be applied in circuits working well over 100 GHz. The band gap of Si–Ge alloys may be tailored between 1·12 and 0·67 eV by changing the composition and using suitable processing conditions. With lower band gap (as compared to silicon), free carrier absorption of infrared radiation can be enhanced, which is an important consideration for solar cells.

In the past, silicon–germanium alloys were prepared, for example, by vacuum hot pressing[1] and melting methods. Recently, there has been an emphasis on silicon–germanium films. And devices, such as heterojunction bipolar transistors[2,3] and heterojunction field effect transistors,[4] have been fabricated. Further, silicon–germanium films are attracting great attention for high performance applications in microelectronics[5–7] as well.

Over the past decade, this laboratory has reported some very surprising findings related to the vast differences observed between the interactions of the electrical field and magnetic field components of 2·45 GHz microwave radiation with matter. The ability to 'separately' interact the E and H fields with solid matter experimentally was first reported in 2001. It is achieved using the E and H fields maxima in a single mode cavity as locations for processing of small samples. This experimental ability resulted in some remarkable observations in understanding the microwave–matter interactions. Thus, for example, it was established that heating in microwave radiation is in many cases[8,9] entirely due to H field absorption (e.g. Co, WC, etc.) and in others entirely due to the E field (e.g. ZnO). In mixed fields, of course, the relative absorptions are a complex function of temperature. Surprisingly, in the common hard ferromagnetic materials (e.g. $BaFe_{12}O_{19}$), it was shown that the starting powder mixtures which normally take several hours to react at about 1100–1200°C, could be completely reacted and homogenised in 5–30 s to form an amorphous phase in H field. Further, the magnetic properties of the same material produced in a multimode, E field and H field were radically different from each other.[10–12]

The authors report here the entirely new results on rapid silicon–germanium alloy formation following the above approach of microwave heating using only the magnetic field in a single mode cavity. A mixture of silicon (75 wt-%) and germanium (25 wt-%) powders was heated in the maximum magnetic field in a TE_{103} single mode 2·45 GHz microwave cavity for 2–5 min, as a result single phase Si–Ge alloy gets formed as revealed by X-ray analysis. This adds to the evidence reported earlier of the generality of the important role the magnetic field plays in microwave processing of materials.

Further, this method of synthesising Si–Ge alloys is unique in several ways: conventionally Si–Ge alloys are prepared by melt and vacuum hot press methods only, which are quite time consuming and complex. In the microwave method described hereunder, a direct reaction of Si and Ge powders was successfully accomplished in a few minutes at ambient pressure. It is a rapid process and results in a single phase material.

Experimental

Materials

Fine powders of silicon (Alfa Aesar, 99·9985% pure, particle size: ~1 μm) and germanium (Cerac, 99·999%

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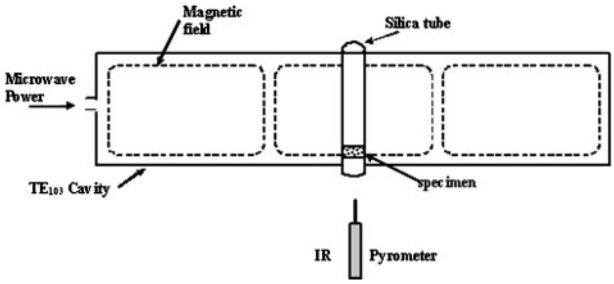
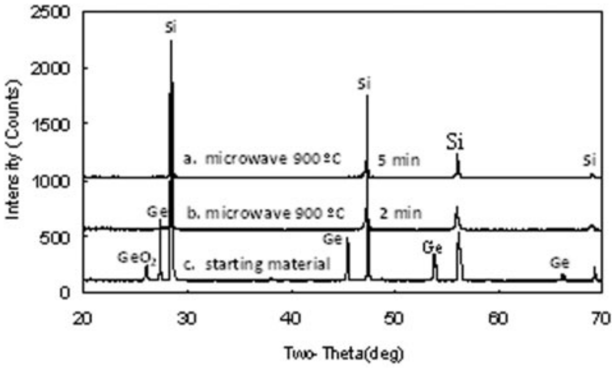


1 Microwave cavity in TE_{103} mode at 2·45 GHz: specimen is located at H_{max} field position



a microwave at 900°C for 5 min; *b* microwave at 900°C for 2 min; *c* starting material

2 XRD patterns of microwave processed in air and untreated mixture of 75%Si+25%Ge

pure, as revealed later, trace amount of germanium oxide, formed possibly due to the exposure to atmosphere, was also present, particle size: −100 mesh) were mixed in a ratio of 75 wt-%Si and 25 wt-%Ge and then ball milled (plastic balls in a Wig-bug mixer) for 10 min. The contamination deriving from the ball mill and balls is negligible because plastic balls and plastic bottles were used. And the ball milling time was very short. Small quantities of the mixed powder were packed either in alumina cylinders open at both ends (o.d.: 6 mm and height: ~4 mm, cut from an alumina tube) or compacted pellets of roughly the same dimensions were used for experimentation.

Microwave heat treatment

The alumina crucible/cylinder with the mixed silicon–germanium powders, or the pellet of the same composition, was heated for specific durations (2–5 min) at the H field maximum using the apparatus described at length elsewhere.[8,9] The alumina crucible was open at one end exposing the sample so that the temperature of the powder is directly measured. The crucible/pellet was inserted into the fused silica tube and positioned at the maximum H field region as can be seen in Fig. 1.

All the experiments were conducted for convenience at ambient pressure in air. One sample was also run in flowing Ar_2+H_2 atmosphere for comparison. The cavity was flushed with Ar_2+H_2 mixture before heating the sample in the cavity. The pellet/powder temperature was recorded using an infrared pyrometer (Raytek, Model Rayma2SCCF) and placed outside the cavity but focused on the surface of the sample. The pyrometer was calibrated using a standard thermocouple in a conventional electrical furnace and the same palletised sample. The XRD patterns were obtained on sample pellets/powders using Scintag PAD V. The SEM and EDS were obtained on Hitachi S-3500N. The particle size of the precursor powder Si was determined using particle size analyser (Malvern Instruments).

Figure 1 schematically depicts the magnetic field distribution in a TE_{103} microwave cavity. A fused silica tube is inserted through the side walls at the centre of the cavity where E and H field maxima are located. The specimen was exposed to only the H field maximum since at the E field maximum, dense plasma is generated before any effective heating takes place. The input power used was 500–800 W and the temperature of the sample was maintained at ~900°C by controlling the input power.

Results and discussion

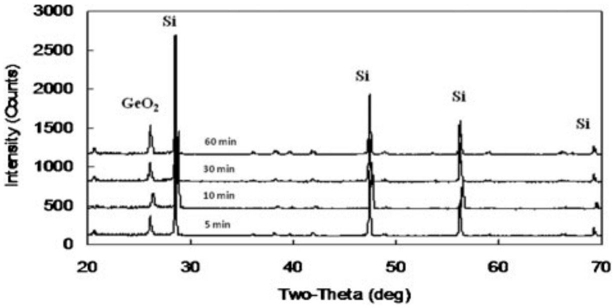
Figure 2 displays X-ray diffraction patterns of microwave processed and raw mixture of starting powders. Figure 2*a* and *b* shows the X-ray diffraction patterns of pellets of 75%Si and 25%Ge mixture reacted for 5 and 2 min respectively in the microwave H field. The germanium gets dissolved into silicon lattice forming an alloy as is evidenced by slight broadening and a shift in silicon peaks as can be seen in Table 1. There is no other phase present in the final product. The situation does not change on heating the mixture for 5 min in microwave H field (Fig. 2*a*). Figure 2*c* exhibits the X-ray pattern of the powder mixture before microwave heat treatment where the peaks corresponding to Si, Ge and GeO_2 (in the metastable quartz form as a minor impurity) are marked (the GeO_2 quartz is no doubt, present in the starting material itself due to partial oxidation of Ge through exposure to the atmosphere).

A set of pellets were also heat treated in a conventional furnace at 900°C (Fig. 3) and 1000°C (Fig. 4) for durations ranging from 5 to 60 min in air, for comparison with the microwave results. The XRD patterns (Figs. 3 and 4) clearly indicate that no Si–Ge alloy is formed in conventional heating. Instead, the germanium gets oxidised forming GeO_2 whose peaks become stronger with increasing heating time and temperature. However, at 1000°C, GeO_2 peak intensity decreases with time. This may be due to partial conversion of GeO_2 (m.p. 1116°C) into a glassy phase.

In the microwave heat treatment, what happens to germanium oxide that was present in the starting material? Germanium oxide is separated from the alloy on heating in H field in the cavity and appears as a thin film of amorphous material on the surface of the pellet. This thin film may also contain the oxidised phase(s) of Si–Ge due to air atmosphere used in the experiment as confirmed by EDS. To confirm it further, pellets of a

Table 1 2θ values of Si peaks recorded by XRD for untreated and MW H field processed Si–Ge mixture in air

(*hkl*)	Starting Si powder	MW H field, 900°C, 2 min	MW H field, 900°C, 5 min
Si(111)	28·520	28·519	28·458
Si(220)	47·380	47·379	47·218



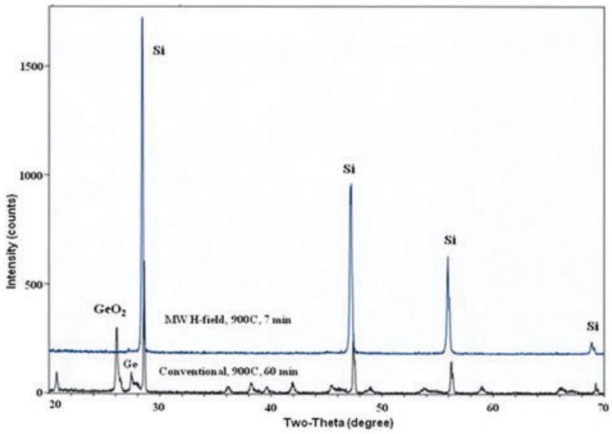
3 XRD patterns of samples conventionally heated at 900°C

mixture of 5 wt-%GeO_2 powder and 95 wt-% of 75%Si + 25%Ge mixture were prepared and heat treated in microwave H field at 900°C for 2 min. The separated white substance from several such heat treated pellets was scraped and collected for further characterisation. The XRD and EDS performed on this material indicated that it contained mainly glassy phase(s) of Ge(+ Si)O_2.

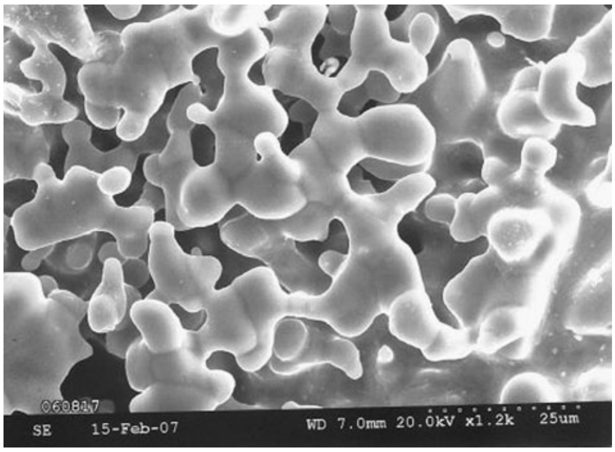
This separation of chemical species, a kind of segregation, in microwave field, has come to our attention for the first time and may play a significant role in microwave processing. Since in microwave processing, the heat flow is from the centre towards the surface, the observed separation of the glassy phase may be the result of reverse diffusion. In addition, the oxide layer perhaps acts as a shield against further oxidation of the constituents. The authors have examined the cross-section of the microwave processed samples and no trace of the white material was detected in the interior of the pellet.

Some of the specimen pellets of the silicon–germanium mixtures were also heat treated in microwave fields under a controlled environment of 51%H_2 and 49%Ar_2. In these samples, the mixed oxides (present in the precursor Ge powder) also got separated/segregated but were in very small quantities, indicating that only the small impurity of GeO_2 originally present in the precursor Ge powder got segregated. The clean pellets were verified to be pure Si–Ge alloy by XRD patterns as can be seen in Fig. 5. Table 2 lists the 2θ values for Si–Ge alloy prepared in Ar + H_2. It is evident that there is a shift in the 2θ values with respect to the pure Si indicating the formation of actual alloy.

Figure 6 displays an SEM image of the microstructure of sintered Si–Ge alloy prepared in Ar_2 + H_2 atmosphere. The microstructure consists of grains of partially



5 XRD patterns of microwave processed in H field and Ar + H_2 atmosphere; conventionally treated mixture of 75%Si + 25%Ge

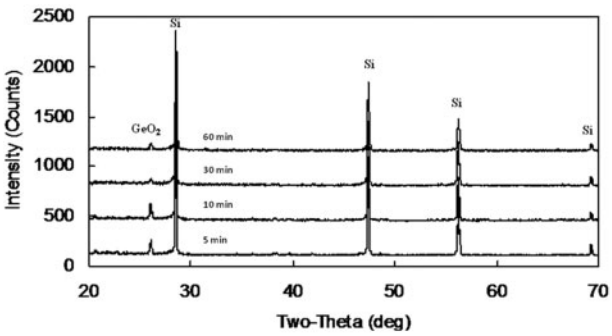


6 SEM image of sintered sample of 75%Si + 25%Ge sample processed in MW H field at 900°C in Ar_2 + H_2 atmosphere for 7 min

sintered material indicating neck formation among individual grains. The EDAX study of various grains showed that they are composed of only Si and Ge metals with the average composition of 75 and 25%. This verifies that almost all of the Ge metal had alloyed with Si lattice and formed a very clean and pure single phase alloy material.

Conclusion

A 2·45 GHz H field microwave exposure can be used to cause useful reactions of various semiconductor combinations not possible with thermal fields alone. A simple method of synthesising Si–Ge alloy from solid state reaction between powder precursors using microwave H field has been demonstrated. The uniqueness of the method lies in the fact that conventionally Si–Ge alloys are prepared by melt and vacuum hot press methods



4 XRD patterns of samples conventionally heated at 1000°C

Table 2 2*θ* values of Si peaks recorded by XRD for untreated and MW H field processed Si–Ge mixture in 51%Ar + 49%H_2 atmosphere

(*hkl*)	Starting Si powder	MW H field, 900°C, 7 min
Si(111)	28·520	28·401
Si(220)	47·380	47·236

only, which are time consuming and complex. In the microwave method as described above, a rapid direct reaction of Si and Ge powders is accomplished at ambient pressure resulting in a single phase material.

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References

1. R. W. Bunce and D. M. Rowe: *J. Phys. D, Appl. Phys.*, 1977, **10D**, 941–946.
2. C. A. King, J. L Hoyt and J. F. Gibbons*: IEEE Trans. Electron. Devices*, 1989, **36**, (10), 2093–2104.
3. G. L. Patton, J. H. Comfort, B. S. Meyerson, E. F. Crabbe, G. J. Scilla, E. de Fresart, J. M. C. Stork, J. Y.-C. Sun, D. L. Harame and J. N. Burghartz: *IEEE Electron. Device Lett.*, 1990, **11**, 171–173.
4. D. A. Webb and M. G. Ward: 'Heterojunction field effect transistors using silicon–germanium and silicon–carbon alloys,' US Patent 6936869, 2002.
5. J. T. Borenstain, N. D. Gerrish, R. White, M. T. Currie and E. A. Fitzgerald: *Proc. Mater. Res. Soc. Symp.*, 2001, **657**, 7.4.1–7.4.6.
6. Thin Films: 'Heteroepitaxial systems', (eds. W. Liu and M. Santos), Vol. 15; 1999, Singapore, World Scientific.
7. E. Kasper and K. Lyertovich (eds.): 'Properties of silicon germanium and silver: carbon'; 2000, London, INSPEC/IEE.
8. J. Cheng, R. Roy and D. Agrawal: *J. Mater. Sci. Lett.*, 2001, **20**, 1561–1563.
9. J. Cheng, R. Roy and D. Agrawal: *Mater. Res. Innov.*, 2002, **5**, 170–177.
10. R. Roy, P. D. Peelamedu, L. Hurtt, J. P. Cheng and D. Agrawal: *Mater. Res. Innov.*, 2002, **6**, 128–140.
11. R. Roy, P. D. Peelamedu, J. P. Cheng, C. Grimes and D. Agrawal: *J. Mater. Res.*, 2002, **17**, 3008–3011.
12. R. Roy, D. Agrawal, R. Peelamedu, Y. Fang and J. Cheng: Proc. 9th Int. Conf. on 'Microwave and high frequency heating', Loughborough, UK, September 2003, Loughborough University, 47–50.