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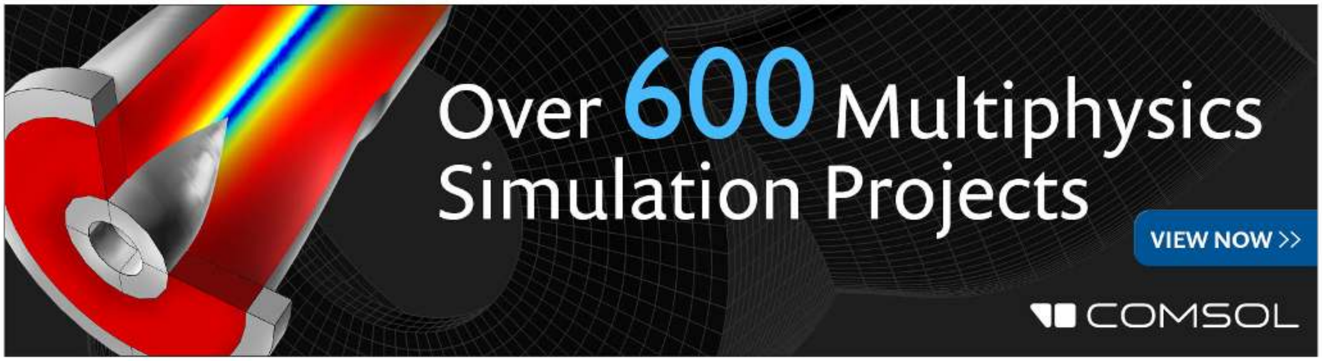

Room-temperature synthesis of copper germanide phase by ion beam mixing

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This letter reports room-temperature synthesis by ion beam mixing of the ϵ_1-Cu_3Ge phase which is a promising candidate for interconnect and contact material in very large scale integrated circuit technology. The resistivity of the mixed sample was found to be nearly the same as the one obtained from thermally prepared films. We briefly discuss the likely mechanisms of phase formation and conclude that reaction kinetics dominates over thermodynamic forces during phase formation. The sequence of phase formation is explained by effective heat of formation rule. © *1995 American Institute of Physics.*

There is a constant search for suitable materials for interconnects and contacts in very large scale integrated circuits (VLSI) because the packing density, speed, etc. are usually limited by interconnects and contact requirements rather than by decreasing active device dimension.[1,2] For example, if the circuit size is scaled by a factor k, the interconnect resistance increases by a factor $1/k$ while the contact resistance increases by $1/k^2$.[3] Thus, the materials to be used for this purpose must possess a low resistivity apart from other favorable properties such as low electromigration, low diffusivity, high corrosion resistance, etc. It has recently been discovered that the ϵ_1-Cu_3Ge phase prepared by solid state reaction possesses most of the desirable properties making it a potential candidate for its use as an interconnect/contact material in the existing GaAs and Si device technology.[1,4] This phase is found to be stable and reproducible and thin films of thickness 100–200 nm have room-temperature resistivity of few $\mu\Omega$ cm, which is even lower than that reported for $CoSi_2$ and $NiSi_2$ epitaxial thin films.[4–6] However, the synthesis of the phase required thermal annealing typically at 400 °C for 30 min. The methods of synthesis using directed energy deposition processes such as ion beam mixing have not yet been explored. For the formation of stable and metastable phases, ion beam mixing has been widely used for its several advantages over solid state reaction such as lower processing temperature and high spatial selectivity.[7,8]

In this letter, we report room-temperature synthesis of the desirable ϵ_1-Cu_3Ge phase by ion beam mixing. The role of reaction kinetics and thermodynamic forces in the mechanism of phase formation have been discussed.

Multilayer structures of Cu and Ge were used to synthesize germanide phase while bilayer structures with or without marker layer at the interface were investigated for understanding the mechanism of mixing. In preparing multilayer samples, alternate layers of Cu and Ge were deposited sequentially on clean quartz substrates without breaking vacuum by the e-beam evaporation system equipped with a digital thickness monitor. For some bilayer structures a thin marker layer of gold of thickness 20 Å was deposited between Cu and Ge layers. The thickness of the individual layers were so adjusted that the overall compositions for bilayer and multilayer configurations were $Cu_{50}Ge_{50}$ and $Cu_{80}Ge_{20}$, respectively.

The mixing was done at room temperature using 1 MeV Kr^+ and Ar^+ for several doses in the range of $(2-20)\times10^{15}/cm^2$. The flux was kept low ($\leqslant 1\times10^{13}$ atoms/cm^2 s^{-1}) to prevent the sample heating during irradiation. For the incident ion energy of 1 MeV, most of the implanted ions pass through the multilayer and bilayer structures. The range and deposited energy F_d of the incident ions were calculated using the TRIM program.[9] The amount of mixing and the composition of the mixed layer were studied by Rutherford backscattering spectrometry (RBS) using 1.5 MeV He^+ beam. The 2 MeV Van de Graaff accelerator at IIT, Kanpur was used for irradiation as well as RBS measurements. RBS spectra were analyzed using computer simulation program RUMP.[10] The RBS spectra of the mixed samples did not show any visible oxygen or carbon concentrations. The copper germanide phases were identified by x-ray diffraction technique using a Cu $K\alpha$ source. The surface topography of the samples observed under the scanning electron microscope did not show any noticeable features before and after mixing. The resistivity measurements were done using the four-probe method. The elastic recoil detection analysis (ERDA) was done to study the hydrogen concentration in the near-surface region of all samples.

The RBS spectrum of the as-deposited multilayer sample is shown in Fig. 1 along with the simulated spectrum. The sample consists of five pairs of copper and germanium layers with an overall thickness of Cu and Ge which are equal to 1550 and 700 Å, respectively. The spectrum of the as-deposited sample shows multipeak structure, however peaks corresponding to individual Cu and Ge layers are not completely resolved because of the small mass difference. The mixing progresses as a function of increasing dose indicated by the decreasing peak to trough ratio of the RBS signals. The irradiations up to a dose of 8×10^{15} Kr^+/cm^2 results in the formation of mixed regions having composition of $Cu_{75}Ge_{25}$ along with unreacted layers of Cu and Ge. For higher doses, the presence of a mixed region having a composition of $Cu_{83}Ge_{17}$ has also been detected. The spectrum after irradiation with Kr ions for a dose of 1

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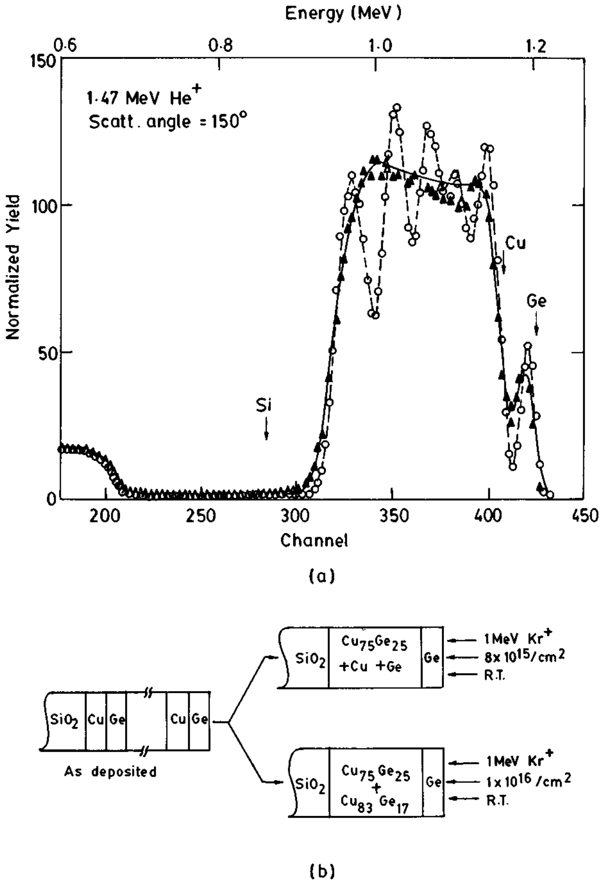

FIG. 1. (a) Rutherford backscattering spectra of multilayers of Cu and Ge on quartz substrate for as-deposited sample (○) and after room-temperature mixing (▲) with 1 MeV Kr$^+$ ions at a dose of 1×10^{16} Kr$^+$/cm^2. The corresponding simulated spectra are shown by dashed line and solid line, respectively. The surface positions of the elements are indicated by arrows. (b) Schematics showing the layer structure of the sample before and after ion beam mixing. The as-deposited structure consists of five pairs of Cu and Ge layers.

$\times10^{16}$ atoms/cm^2 is shown in Fig. 1. This spectrum could be simulated using the structure shown in Fig. 1(b) consisting of two compositions $Cu_{75}Ge_{25}$ and $Cu_{83}Ge_{17}$ in the mixed region. These compositions have been identified to corresponding Cu_3Ge (ϵ_1 phase) and Cu_5Ge (ζ phase)[11] as shown by the x-ray diffraction spectra depicted in Fig. 2. Corresponding to the RBS results, the presence of Cu_3Ge phase has been detected up to a dose of 8×10^{15} Kr$^+$/cm^2, while at higher doses a small amount of the ζ phase is also observed. The occurrence of both Cu_3Ge[5,12] and ζ phases[11] were expected in ion mixing since those are the only phases observed during thermal annealing experiments. The resistivity of the mixed layer is typically 20 $\mu\Omega$ cm which is very close to the value obtained by Aboelfotoh *et al.* for 200 nm thermally prepared thick film.[5] It is to be noted that the top Ge layer does not take part in the reaction at the same rate as the subsequent layers. This may be due to the lower deposited energy density F_d value at the surface. Another possible reason could be due to the presence of hydrogen in the top layer detected by ERD measurements. A detailed study is required to investigate the role of hydrogen in the mixing process.

Similar mixing effects were also observed in the samples irradiated with Ar ions. However, the rate of mixing is lower as compared to the Kr ion irradiation for the same incident energy because of the lower F_d value. To give a comparison, the mixing obtained with Ar ions at a dose of 1×10^{16} atoms/cm^2 is almost the same as that obtained with Kr ions at a dose of 4×10^{15} atoms/cm^2.

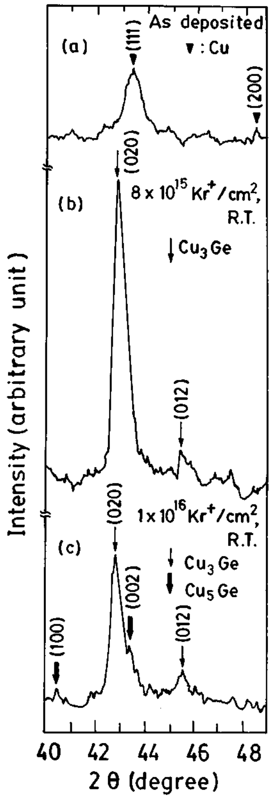

FIG. 2. X-ray diffraction patterns for (a) as-deposited Cu/Ge multilayer samples and after room-temperature ion beam mixing at a dose of (b) 8×10^{15} Kr$^+$/cm^2 (c) 1×10^{16} Kr$^+$/cm^2.

It is now well-established that ion beam mixing at low temperature is governed by ballistic collision and global[13–15] or local thermal spike[16] processes. At a higher temperature, radiation enhanced diffusion (RED) plays a dominant role.[13,17] The critical temperature T_c for radiation enhanced diffusion in this system is calculated as 386 K which is well above the room temperature.[17] Therefore, RED has little contribution to the room-temperature mixing. Our bilayer mixing results show that the square of the mixed thickness varies linearly with ion dose. This signifies that mixing in this system is a diffusion controlled process. The mixing efficiency is found to be 10.75 nm^5/keV. Furthermore, a detailed analysis using existing models[13–16] shows that the mixing is occurring via global cylindrical spikes.

The formation of a phase depends on the mobilities of the reacting species and the temperature during irradiation. In a solid state reaction the kinetic constraints play a dominant role, whereas in ion beam mixing it is normally assumed that the kinetic restriction is relaxed. Thus, both the reaction kinetics as well as the thermodynamic driving forces play an active role during mixing.[18] Extensive efforts have been made experimentally as well as theoretically to understand the effect of thermodynamic driving forces and the kinetics of phase formation during ion beam mixing and thermal annealing in metal/metal and metal/Si thin films.[7,8,15,18,19] It has been found that if the temperature is low enough for one of the reacting species to be mobile then metastable, amorphous or simple crystalline structure would form, whereas for irradiation at higher temperature, when both the species are mobile, the stable crystalline phase would be produced.[7,20] In order to identify the mobile species in this system we have performed the mixing of Cu–Ge bilayers with a marker at the interface. The results of these marker experiments show that Cu is the dominant moving species across the interface during room-temperature irradiation. Thereby, Cu atoms move through the germanide phase to react with Ge at the interface. The movement of the marker has been calculated using the models of Auner *et al.*[21] as well as Chae *et al.*[22] developed for metal/Si systems. According to Auner's model preferential atomic movement of Ge atoms from the top layer into the Cu layer should occur, whereas Chae's model would predict isotropic movement for this system as in Pd/Co and Pd/Si. However, our results show a different trend. Interestingly, in thermal annealing studies d'Heurle and Gupta.[11] have found that at low temperature only Cu atoms move for the formation of the Cu_3Ge phase and both move for the formation of the ζ phase at the temperature between 200 and 250 °C. A detailed analysis of the experimental results of bilayer mixing will be reported separately.

The formation of the crystalline phase in this system is expected from the structure difference rule[8] which states that the reacting species having the same crystalline structure produce a crystalline phase. To predict the sequence of phase formation, the heat of formation rule[7] has been proposed. According to this rule the phase with the most negative heat of formation has the largest chemical driving force and therefore, would form first.[7] The heat of formation of the ϵ_1-Cu_3Ge phase is -4 kJ/g at.[23] whereas the value for the ζ phase is not available. From the phase diagram we find that the melting temperature of the ζ phase is slightly higher than that of the Cu_3Ge phase signifying that the heat of formation of the ζ phase should be higher than that of the Cu_3Ge phase. Thus, according to the above rule the ζ phase should form first. However, in our experiments it is the Cu_3Ge phase which forms first. Similar deviations from the heat of formation rule have been reported in many metal/Si systems.[18] In all those cases, it is assumed that in determining the sequence of phase formation, kinetic factors dominate over the thermodynamic driving forces. However, it would be more appropriate in this case to use the effective heat of formation rule as proposed by Pretorious *et al.*[24] since it takes into account both the kinetics and thermodynamic forces. The factor which modifies the heat of formation is a ratio of the effective concentration of the limiting element to the compound concentration of the limiting element. In the present case, as discussed above, Cu is the moving species and it is also the limiting element which decides the effective heat of formation. Due to the nonavailability of experimental thermodynamic data for the ζ phase we could make only approximate calculations which show that the magnitude of heat of formation for the ζ phase is less than that of Cu_3Ge phase and therefore the Cu_3Ge phase should form first which is in accordance with our experimental observation.

In summary, we have shown that the ϵ_1-Cu_3Ge phase can be produced at room temperature by ion beam mixing of Cu–Ge multilayer structure by 1 MeV Kr and Ar ions. The resistivity of this phase is comparable to those produced by thermal annealing. Cu is found to be the dominant moving species controlling phase formation and the sequence of the phase formation can be explained on the basis of the effective heat of formation rule.

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[1] M. O. Aboelfotoh, C. L. Lin, and J. M. Woodall, Appl. Phys. Lett. **65**, 3245 (1994).

[2] J. B. Butcher, in *Proceedings of the 17th Yugoslav Conference on Microelectronics*, edited by M. Stojadinovic (Elsevier, Oxford, 1989), Vol. 1, p. 1.

[3] *VLSI Electronics Microstructure Science*, edited by N. G. Einspruch (Academic, New York, 1981), Vol. 1, p. 18.

[4] L. Krusin-Elbaum and M. O. Aboelfotoh, Appl. Phys. Lett. **58**, 1341 (1991).

[5] M. O. Aboelfotoh, H. M. Tawancy, and L. Krusin-Elbaum, Appl. Phys. Lett. **63**, 1622 (1993).

[6] M. O. Aboelfotoh and H. M. Tawancy, J. Appl. Phys. **75**, 2441 (1994).

[7] G. S. Was, Prog. Surf. Sci. **32**, 211 (1990).

[8] B. X. Liu, Phys. Status Solidi A **94**, 11 (1986).

[9] J. P. Biersack and L.G. Haggmark, Nucl. Instrum. Methods **174**, 257 (1980).

[10] L.R. Doolittle, Nucl. Instrum. Methods B **9**, 344 (1985).

[11] F. M. d'Heurle and J. Gupta, Appl. Surf. Sci. **73**, 214 (1993).

[12] S. Q. Hong, C. M. Comrie, S. W. Russell, and J. W. Mayer, J. Appl. Phys. **70**, 3655 (1991).

[13] Y.-T. Cheng, Mater. Sci. Rep. **5**, 45 (1990).

[14] W. Bolse, Nucl. Instrum. Methods B **80/81**, 137 (1993).

[15] J. Desimoni and A. Traverse, Phys. Rev. B **48**, 13266 (1993).

[16] P. Borgesen, D. A. Lilienfeld, and H. H. Johnson, Appl. Phys. Lett. **57**, 1407 (1990).

[17] Y.-T. Cheng, X.-A. Zhao, T. Banwell, T. W. Workman, M.-A. Nicolet, and W. L. Johnson, J. Appl. Phys. **60**, 2615 (1986).

[18] W. Xia, C. A. Hewett, M. Fernandes, S. S. Lau, and D. B. Poker, J. Appl. Phys. **65**, 2300 (1989).

[19] A. H. Reader, A. H. van Ommen, P. J. W. Weijs, R. A. M. Wolters, and D. J. Oostra, Rep. Prog. Phys. **56**, 1397 (1992).

[20] T. L. Alford, P. Borgesen, and J. W. Mayer, Appl. Phys. Lett. **58**, 1848 (1991).

[21] G. W. Auner, Y.-T. Cheng, M. H. Alkaisi, M. M. Karmarkar, and K. R. Padmanabhan, Nucl. Instrum. Methods B **59/60**, 506 (1991).

[22] K. H. Chae, J. H. Song, S. M. Jung, H. G. Jang, J. J. Woo, K. Jeong, C. N. Whang, Y. J. Oh, and H. J. Jung, J. Appl. Phys. **73**, 4292 (1993).

[23] S. V. Meschel and O. J. Kleppa, Metall. Trans. A **22**, 2162 (1991).

[24] R. Pretorius, A. M. Vredenberg, F. W. Saris, and R. D. Reus, J. Appl. Phys. **70**, 3636 (1991).