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Ion-induced room temperature synthesis of low resistive nickel germanide phase

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Low resistivity Ni_2Ge phase, a promising candidate as a contact and interconnect material for very large scale integrated circuit applications, has been synthesized by MeV ion beam mixing using Kr and Ar ions at and above room temperatures. Thin films of this phase produced by ion beam mixing show resistivity comparable to the one produced by thermal annealing and is much lower than that of many important silicides. The critical temperature which marks the beginning of the temperature dependent mixing is 326 K. The room temperature mixing efficiency for this system is found to be about an order of magnitude higher than the value predicted by any of the existing ballistic and spike models. The crystalline nature of the mixed region and the occurrence of the Ni_2Ge phase have been discussed. © *1998 American Institute of Physics.* [S0021-8979(98)00304-1]

The device scaling which is used to improve chip density and performance of very large scale integrated (VLSI) circuits results in new and stringent requirements on materials used for gate interconnects, contact, and metal interconnects.[1,2] In general, the scaling cannot be realized without a reduction in the resistance of contact and interconnect materials. Several other properties such as electromigration resistance, thermal stability, etc. also become important. Thus, there is a constant search for suitable contact/interconnect materials for VLSI technology. In this regard, the low resistive (6–8 $\mu\Omega$ cm) copper germanide Cu_3Ge phase has attracted the attention of several researchers.[3–9] Recently, we have reported[6,7] the room temperature synthesis of Cu_3Ge phase by ion beam mixing. This phase shows good thermal stability[3] and yields a very low contact resistance with n-GaAs.[5] However, it has been reported that the Cu_3Ge phase does not grow epitaxially[8] on GaAs and it reacts with Si at 570 K.[9] These limitations of the Cu_3Ge system lead to a search for those germanides which have favorable properties. Nickel germanide (Ni_2Ge) is one such material of this category. In our preliminary investigations[10] we have shown that the thermally prepared Ni_2Ge phase has a resistivity of 23 $\mu\Omega$ cm which is lower than the resistivity of many silicide phases like $NiSi_2$, $FeSi_2$, PtSi, $ZrSi_2$, etc.[2] It may be noted that the Ni_2Ge phase has orthrorhombic structure similar to many epitaxially[1] grown silicide phases like $FeSi_2$, PtSi, $ZrSi_2$, etc. on a Si substrate. Thus, Ni_2Ge is expected to offer definite advantages over Cu_3Ge and many other silicide phases.

In this communication we report, for the first time, on the synthesis of low resistivity Ni_2Ge phase by MeV ion beam mixing which has emerged as a powerful processing technique to synthesize both equilibrium and nonequilibrium phases at relatively low temperatures. We will show that the experimentally determined critical temperature above which ion beam mixing exhibits temperature dependence, and the nature of the phase formed, can be satisfactorily predicted on the basis of the existing empirical rules. However, the models generally used to explain mixing efficiencies are found to be inadequate to explain experimental results.

Alternate layers of Ni and Ge were sequentially deposited, without breaking vacuum, on clean quartz substrates to prepare multilayer or bilayer structures to study the phase formation and mixing mechanism, respectively. A few bilayer films of Ni/Ge were prepared with a thin marker layer of gold of thickness 1 nm between Ni and Ge layers. The thickness of the individual layers were so adjusted that the overall compositions for bilayer and multilayer configurations were $Ni_{50}Ge_{50}$ and $Ni_{66}Ge_{34}$, respectively.

The ion beam mixing experiments were performed at sample temperatures ranging from 100 to 450 K using 1 MeV Kr^+ and Ar^+ for several doses in the range of $(2-20)\times 10^{15}$ atoms/cm^2. The flux was kept low ($\leq 1 \times 10^{13}$ atoms/cm^2 s^{-1}) to prevent the sample temperature rise during irradiation. The range and deposited energy F_d of the incident ions were calculated using the TRIM92 code.[11] Some of the as-deposited samples were thermally treated in high vacuum at 450–600 K to induce solid state reaction. The surface topography of the samples observed under scanning electron microscope did not show any noticeable features before and after mixing or thermal annealing. Various techniques like Rutherford backscattering spectrometry (RBS), x-ray diffraction (XRD), and four probe resistivity measurement techniques were used to characterize the as-deposited, ion beam mixed, and thermally treated samples. RBS spectra were analyzed using the computer simulation program RUMP.[12]

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 Ni and Ge layers with an overall thickness of Ni and Ge equal to 170 and 120 nm, respectively. The spectrum of the as-deposited sample shows multi-peak structure. The peaks corresponding to individual Ni and Ge layers are not completely resolved because of the

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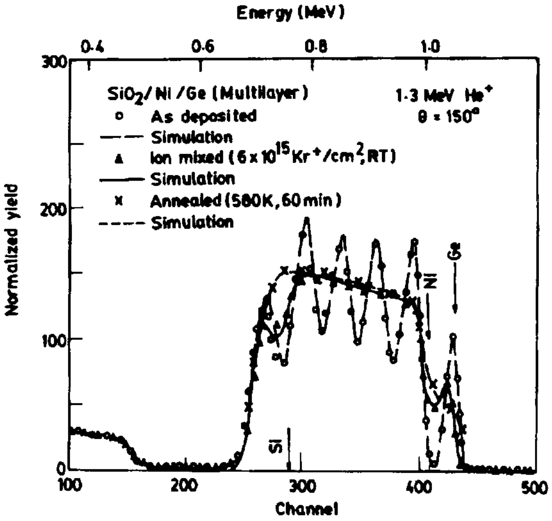

FIG. 1. RBS spectra of multilayers of Ni and Ge on quartz substrate for as-deposited sample and after room temperature mixing with 1 MeV Kr^+ ions at a dose of 6×10^{15} $\mathrm{Kr}^+/\mathrm{cm}^2$. The RBS spectum after thermal annealing at 580 K for 1 h is also shown for comparison. The surface positions of the elements are indicated by arrows.

small mass difference. The RBS spectrum after room temperature (RT) irradiation with Kr ions for a dose of 6×10^{15} $\mathrm{Kr}^+/\mathrm{cm}^2$ along with the simulated spectrum are also shown in Fig. 1. This spectrum could be simulated using the structure consisting of a single layer of thickness 240 nm and composition $\mathrm{Ni}_{66}\mathrm{Ge}_{34}$ for the mixed region. This composition corresponds to the $\mathrm{Ni}_2\mathrm{Ge}$ phase present in the Ni–Ge equilibrium phase diagram.[13] Irradiations up to a dose of 1×10^{16} $\mathrm{Kr}^+/\mathrm{cm}^2$ in the temperature range of 100–450 K produce mixed regions of the same composition. However, mixing proceeds much rapidly above RT irradiation. Irradiations with Ar ions also lead to the formation of mixed region having composition of $\mathrm{Ni}_2\mathrm{Ge}$, although in this case the mixing occurs at a slower rate as compared to Kr irradiations.

The effect of thermal reaction at 580 K for 1 h on the as-deposited sample is also shown in Fig. 1 for comparison. It clearly demonstrates that the thermal annealing of the as-deposited sample at 580 K results in a uniform homogeneous film of composition $\mathrm{Ni}_{66}\mathrm{Ge}_{34}$ similar to the one produced by ion beam mixing at RT.

The resistivity of the ion beam mixed layer is typically about 40–50 $\mu\Omega$ cm, whereas the one prepared by thermal annealing is about 20–25 $\mu\Omega$ cm. The higher value of resistivity in the ion beam mixed films is attributed to the presence of radiation induced defects.

Conventional x-ray diffraction measurements as well as those performed in Seeman–Bohlin geometry did not show any peak for the as-deposited Ni/Ge multilayer sample indicating the amorphous/highly disordered state of the individual Ni and Ge layers.[14,15] The x-ray diffraction spectra (not shown) of the samples irradiated at RT for various doses and the thermally annealed samples show the presence of the $\mathrm{Ni}_2\mathrm{Ge}$ phase. Irradiations performed at 100 K also indicate formation of the $\mathrm{Ni}_2\mathrm{Ge}$ phase but the x-ray peaks are very weak in this case.[16]

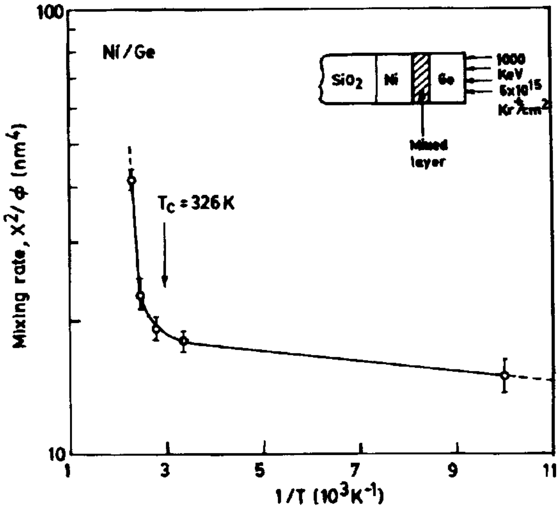

FIG. 2. The variation of mixing rate for Ni/Ge bilayer system as a function of reciprocal of substrate temperature for a dose of 6×10^{15} $\mathrm{Kr}^+/\mathrm{cm}^2$.

Information regarding the growth kinetics, i.e., irradiation dose (Φ) and temperature (T) dependences of the thickness of the mixed layer (X), has been obtained from ion beam mixing experiments performed using bilayer sample structure. The ion beam mixing at room temperature shows that the square of the mixed thickness (X^2) varies linearly with Φ in the case of both Kr and Ar irradiations. It may be noted that the squared thickness of the thermally reacted layers is also proportional to the annealing time suggesting that ion mixing in this system is like a diffusion controlled process.[7] The room temperature mixing rate (X^2/Φ) is found to be linearly proportional to the energy F_D, deposited in hard collisions. The linear dependence gives a mixing efficiency ($X^2/\Phi\ F_D$) of 11.3 nm^5/keV. The variation of mixing rate as a function of $1/T$ is shown in Fig. 2. This shows that the mixing is independent of temperature up to 326 K. This is the critical temperature (T_c) for the Ni/Ge system above which the mixing rate increases rapidly. The value of T_c calculated from the model[17] of de Reus *et al.* is 414±75 K, which is in reasonable agreement with our experimental results. The temperature dependent region yields an activation energy of 0.3 eV.

For the calculation of mixing efficiency various phenomenological models have been reported in the literature.[18–22] The model of Sigmund and Gras-Marti,[18] which uses only ballistic properties of the incident ion and target materials, yields a value of 0.22 nm^5/keV for the present case. The calculations performed using other models,[19–21] which incorporate the effect of thermal spikes and thermodynamic parameters, yield theoretical mixing efficiencies in the range of 0.25–1 nm^5/keV. Thus values calculated using the the current models are about an order of magnitude lower than the experimental value. A careful study of the calculated and experimental values for many systems reported in the literature[7,22] clearly point out that when the systems under consideration are highly reactive (viz. Ni/Si, Pd/Si, Cu/Ge, Co/Ge, etc.) the experimental mixing rates for such systems are always higher than those predicted by the above mentioned models. Recently we have developed a model to successfully explain the high mixing rates in Cu/Ge, Co/Ge, and Ni/Si systems.[7,16] According to this model, in the presence of nonoverlapping/local spikes, the mixing rate across the interface of a bilayer system consisting of elements A and B can be written as[7]

$$\frac{X^2}{\Phi}\Big|_{\text{loc}}^{\text{com}} = K_s\left(\frac{C_A}{a/(a+b)}+\frac{C_B}{b/(a+b)}\right)\frac{2F_D Z_{\text{ave}}^{1.77}}{C^{5/3}\Delta H_{\text{coh}}^2}, \tag{1}$$

where $K_s = 0.95$ Å^3 eV is the proportionality constant, F_D is the deposited energy due to primary and secondary collisions, Z_{ave} is the average atomic number, ΔH_{coh} is the average cohesive energy, C_A and C_B are the atomic densities of elements A and B, respectively, and C is the atomic density of the compound A_aB_b. Here the term within the paranthesis is the compound formation enhancement factor and the term outside the paranthesis is due to the local spikes. The mixing rate for the present system calculated from the above relation is 9.3 nm^5/keV, which is in close agreement with our experimental results. It should be noted that this kind of high growth rate of mixed layer at relatively low temperature for a highly reactive system[7,22] such as silicides, germanides, etc. must be viewed differently from those systems where solid solutions or amorphous phase is produced under ion bombardment prior to the formation of compounds. In the latter case, the long range atomic migration is necessary. However, in the reactive systems (as in the present case) where the diffusive flux of the reacting species is controlled by the reaction rate, such barriers are either absent or negligible such that the systems undergo structural relaxation producing a stable compound. The role of ion irradiation is to maintain the required flux of the reacting species for incorporation into the compound at the reacting interface.

Various empirical rules based on the structure of the constituent elements,[23] atomic radii of the interacting species,[24] etc., have been proposed in the literature to predict the amorphous or crystalline nature of the final phase synthesized by ion bombardment. Since both Ni and Ge have fcc structure and their atomic radii are also not very different (ratio $r_{\text{Ge}}/r_{\text{Ni}} = 0.98$), it is expected that the Ni/Ge system should yield a crystalline phase by ion beam mixing. This is in accordance with the observation. Of further importance is the understanding of the first and subsequent phase formation in the case where both ion beam mixing and thermal annealing are important. The equilibrium phase diagram[13] of the Ni/Ge system shows three stable phases, namely Ni_2Ge, NiGe, and Ni_3Ge. According to the heat of formation rule[25] the phase with the most negative heat of formation has the largest chemical driving force and hence would form first. The heat of formation for the above mentioned phases are -37, -32, and -25 kJ/mole, respectively. Therefore, in this case Ni_2Ge, which has the largest negative heat of formation, is expected to form first. By using a more rigorous approach of concentration controlled phase selection[16,26] it can be shown that Ni_2Ge has the largest effective negative heat of formation across the reacting interface and hence it synthesizes first. Thus, the prediction of these models is in accordance with our ion beam mixing and thermal annealing experimental results.

In summary, we have shown that a low resistivity Ni_2Ge phase has been synthesized by MeV ion beam mixing using Kr and Ar ions at and above room temperature. This phase produced by ion mixing and thermal annealing exhibits lower resistivity than many important silicides. The critical temperature which marks the beginning of the temperature dependent mixing is 326 K. The room temperature mixing efficiency is 11.3 nm^5/keV and is far above the value predicted by ballistic and spike models. The occurrence of the first Ni_2Ge phase and crystalline nature of the mixed region are understood on the basis of existing empirical models.

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