

Temperature-dependent ion mixing and diffusion during sputtering of thin films of CrSi₂ on silicon

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Measurements of sputtering yields and composition profiles have been carried out using backscattering spectrometry for samples of CrSi₂ on Si irradiated with 200-keV Xe ions. When the CrSi₂ layer is thinner than the ion range, the sputtering yield ratio of Si to Cr increases from 3.5 for room-temperature irradiation to 65 at 290 °C. For a thick sample, the corresponding increase is from 2.4 to 4.0 only. These changes are explained in terms of a rise in the Si surface concentration at 290 °C. The driving force for this process seems to be the establishment of stoichiometric CrSi₂ compound. Transport of Si to the surface is by ion mixing in the thin sample and thermal diffusion through the thick layer.

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Evidence for the activation of fast transport processes in solid compound films was recently found in ion mixing experiments with some metal silicides (NbSi₂,¹ CrSi₂,² Ni₂Si³). In those experiments, the atomic mixing of metal layers with a silicon substrate was enhanced greatly when the irradiation was carried out at elevated temperatures. The possibility that the same processes might also affect sputtering from these silicides motivated the present investigation.

In this letter we present results of measurements of partial sputtering yields and compositional changes in samples of CrSi₂ sputtered by high-energy Xe⁺ ions at room temperature and at 290 °C.

Samples were prepared by successively vacuum-evaporating layers of Si and Cr on SiO₂ substrates and annealing them at 500 °C to form CrSi₂. For all samples, the amount of Si deposited was more than that needed to consume all of the Cr in the reaction, with the result that a layer of unreacted Si remained between the silicide and the substrate. One set of samples consisted of 370 Å of CrSi₂ (denoted *t_a*) on 1000 Å of Si and the other of 1800 Å of CrSi₂ (denoted *t_b*) on 580 Å of Si. A 1 cm × 1 cm area of each sample was irradiated with 200-keV Xe⁺ ions to a dose of 5 × 10¹⁶ atoms/cm². These ions have a projected range of about 450 Å in CrSi₂, which is larger than *t_a*, but ~4 times less than *t_b*. A band of carbon foil was placed in a semicircle in front of each sample to collect the sputtered material. The samples and carbon collectors were analyzed by backscattering (BS) spectrometry of 1.5-MeV ⁴He⁺ ions. The sputtering yields of Si and Cr were determined both from the amounts of material collected on the carbon foils (assuming axial symmetry) and from the loss of the two elements from the irradiated portions of the samples. Composition profiles were obtained from the relative heights of Si and Cr signals in the BS spectra (for more details see Ref. 4).

Table I summarizes the sputtering yield calculations. Here the average sputtering yield of element A is defined by $\bar{S}_A = \text{total number of A atoms sputtered, divided by the total number of incoming ions}$. In all cases, data obtained

from the collector and from the sample agreed to within experimental uncertainties.

Figure 1 presents the Cr concentration profiles calculated from the BS spectra for the two sample configurations after sputtering. The fractional atomic concentration of Cr at the surface (C_{Cr}^s) as obtained by extrapolating these profiles to zero depth is given in Table I.

From Table I we see that the sputtering yields ratios $\bar{S}_{Si}/\bar{S}_{Cr}$ increase with temperature for both sample configurations. However, the effect is very much larger in the thin sample. As the table shows, this temperature effect is due mainly to the sharp reduction of the sputtering yield of Cr. From Fig. 1 we also see that there are major differences in the profiles of the two samples after irradiation at the same conditions. One obvious conclusion from these differences is that the large drop in Cr yield from the thin sample at the high temperature is not the result of an external cause like excessive beam heating or surface contamination (oxygen, carbon) since such an effect, if present, should influence both thin and thick samples alike.

We now analyze the results and show first that our measured surface concentrations are consistent with the notion that the sputtering process itself is temperature independent and is not responsible for the observed effects.

TABLE I. Summary of experimental results.

Sample	370 Å CrSi ₂		1800 Å CrSi ₂	
	20	290	20	290
Temperature (°C)				
\bar{S}_{Si}	2.8 ± 0.2	3.3 ± 0.3	2.4 ± 0.3	3.2 ± 0.3
\bar{S}_{Cr}	0.8 ± 0.2	0.05 ± 0.05	1.0 ± 0.2	0.8 ± 0.2
$\bar{S}_{Si}/\bar{S}_{Cr}$	3.5	65	2.4	4.0
C_{Cr}^s ^a	0.33	0.14	0.45	0.33
\bar{C}_{Cr}^s ^b	0.40	0.05	0.49	0.27

^a Extrapolated from profiles of Fig. 1.

^b Estimated values assuming the sputtering yield is proportional to the surface concentration. See text for details.

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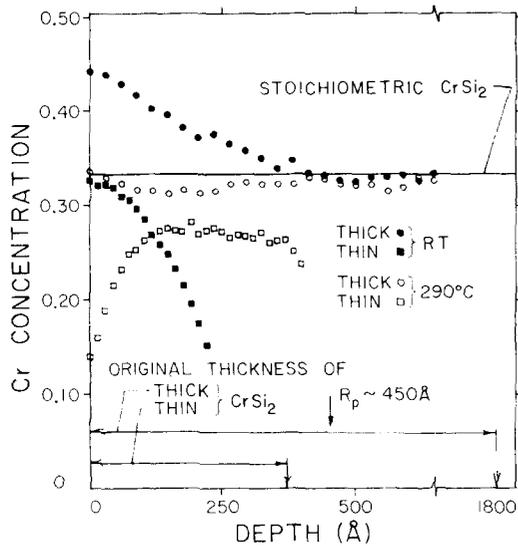


FIG. 1. Depth profiles of the Cr concentration in the irradiated samples. The profiles were calculated from the relative heights of the Si and Cr signals in the backscattering spectra. The depth scale was calculated for stoichiometric CrSi_2 .

Instantaneous sputtering yield ratios are given by

$$\begin{aligned} \frac{S_{\text{Si}}}{S_{\text{Cr}}} &= \frac{Y_{\text{Si}}}{Y_{\text{Cr}}} \frac{C_{\text{Si}}^s}{C_{\text{Cr}}^s} \\ &= \frac{Y_{\text{Si}}}{Y_{\text{Cr}}} \frac{1 - C_{\text{Cr}}^s}{C_{\text{Cr}}^s}, \end{aligned} \quad (1)$$

where Y_{Si} and Y_{Cr} are sputtering probabilities (which, for single element targets are identical to the sputtering yields S). The value of $Y_{\text{Si}}/Y_{\text{Cr}}$ at room temperature is known to be 2.3 from measurements of steady-state sputtering of 1500 Å CrSi_2 by 100-keV Xe^+ ions.⁴ When we substitute this value, and the average sputtering yields from Table I in Eq. (1), we can estimate the expected surface concentrations of Cr, \bar{C}_{Cr}^s , which are listed in the last row of the table. These values are in general agreement with the measured concentrations C_{Cr}^s (see Table I). The remaining differences can arise from several sources: (1) by using average sputtering yields in Eq. (1), we actually estimate the average surface composition during sputtering while C_{Cr}^s is the measured final composition; (2) the depth resolution in our measurements is about 80 Å, so that changes in composition on a smaller scale are smoothed out and cannot be measured accurately; (3) the sputtering probabilities and their ratio may depend (weakly⁵) on the Xe energy. From the generally good agreement of this estimate, we conclude that the sputtering probability ratio $Y_{\text{Si}}/Y_{\text{Cr}}$ is constant in all the cases studied here. The inference is that the sputtering mechanism does not change significantly with temperature either.

Since all the changes in sputtering yields can be attributed to changes in surface composition, we now consider the temperature-dependent processes that determine this composition. At elevated temperatures, the bulk compositions are quite uniform. This fact indicates that chemical driving forces (formation of equilibrium phases) and the necessary atomic mobility are determining factors. A similar conclusion is reached for the ion mixing of Si and Cr bi-

layers, where the intermixing rate at 270 °C is much higher than at room temperature and the mixed layer consists of polycrystalline CrSi_2 .² Also, the rate of mixing is thermally activated which proves that the mixing process extends in time much beyond the duration of an individual collision cascade ($\sim 10^{-12}$ s).⁶ The mixing may thus be viewed as an equilibration process of a volume of excited material that surrounds the track of a penetrating particle and extends to a depth at which the density of deposited energy is appreciable. Applied to the present experiment, this means that when the ion range approaches or penetrates into the underlying silicon layer, Si is mixed into the silicide. As the mixed material relaxes to the equilibrium state appropriate to the sample temperature, this excess silicon must segregate out to grain boundaries of the CrSi_2 phase and to the surface. For the thin sample, we can estimate the amount of excess Si in the bulk as ~ 7 at. % from Fig. 1. If the size of CrSi_2 grains is comparable to the thickness of the layer (~ 400 Å), this excess Si corresponds to a layer of ~ 50 Å around the grains. This estimate is consistent with the measured profile (see Fig. 1).

In electron diffraction measurements on the thin sample after irradiation at 290 °C, we find that it contains polycrystalline CrSi_2 . This result agrees with the concept of phase separation following the mixing of Si in the silicide, however, it does not supply conclusive evidence that Si precipitation to grain boundaries takes place.

For the thick sample, the amount of Si mixed into the silicide from the underlying layer is expected to be much smaller and, apparently, is just enough to compensate for the preferential sputtering of Si from the surface. The result is that the composition remains nearly stoichiometric (Fig. 1).

The fact that stoichiometric conditions are established continuously in our samples at 290 °C means that steady-state sputtering, where the ratio of sputtered atoms equals the bulk composition, can never be reached since that requires the surface to become rich in Cr (the lower sputtering probability element⁷). In this respect, our results differ from previous experiments on temperature effects in sputtering. Such experiments were performed with alloys that form complete series of solid solutions (Ni-Cu ,⁸⁻¹⁰ Au-Pd ,¹⁰ Ag-Au ¹⁰). Since there are no stable compounds in these alloys, there is no driving force for maintaining uniform compositions. Indeed, steady-state sputtering could be reached in all those cases. The only effect of elevated temperature was to increase the (radiation-enhanced) diffusion coefficient and thereby also the time needed to reach steady-state and the depth of the altered layer.

In a recent study, Dumke *et al.*¹¹ found that the sputtering yield ratio of In to Ga from the eutectic alloy increased by a factor of ~ 30 when the temperature was raised above the melting point. This rise is explained as the result of thermal segregation of In to the outermost atomic layer in the liquid. It is interesting to note that in the present work, a comparable change was observed by raising the sample temperature only to ~ 0.3 of the melting point. The possibility that the sputtering yield of one element in a thin compound film will be drastically reduced and a surface layer will be retained, may have an important implication for cases where sputter erosion is used to obtain depth composition profiles.

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¹S. Matteson, J. Roth, and M-A. Nicolet, *Radiat. Eff.* **42**, 217 (1979).

²J. W. Mayer, B. Y. Tsaur, S. S. Lau, and L. S. Hung, *Nucl. Instrum. Methods* **182/183**, 1 (1981).

³L. S. Wieluński, B. M. Paine, B. X. Liu, C-D. Lien, and M-A. Nicolet,

Phys. Status Solidi A **72**, 399 (1982).

⁴R. Fernandez, U. Shreter, and M-A. Nicolet, *Nucl. Instrum. Methods* (in press).

⁵P. Sigmund, *Phys. Rev.* **184**, 383 (1969).

⁶S. Matteson and M-A. Nicolet, in *Annual Review of Materials Science*, edited by R. A. Huggins (Annual Review of Materials Science, Palo Alto, 1983), Vol. 13, p. 339.

⁷P. S. Ho, *Surf. Sci.* **72**, 253 (1978).

⁸N. Q. Lam and H. Wiedersich, in *Metastable Materials Formation by Ion Implantation*, edited by S. T. Picraux and W. J. Choyke (Elsevier, New York, 1982), p. 35.

⁹H. Shimizu, M. Ono, N. Koyama, and Y. Ishida, *J. Appl. Phys.* **53**, 3044 (1982).

¹⁰D. G. Swartzfager, S. B. Ziemecki, and M. J. Kelley, *J. Vac. Sci. Technol.* **19**, 185 (1981).

¹¹M. F. Dumke, T. A. Tombrello, R. A. Weller, R. M. Hansley, and E. H. Cirlin, *Surf. Sci.* (in press).

Growth of metastable $\text{Cu}_{1-x}\text{Cr}_x$ solid solutions by ion mixing during bias-sputter deposition

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The Cu-Cr system exhibits a miscibility gap in the liquid and has essentially no solid solubility. However, using low energy, < 160 eV, Ar^+ ion bombardment of the growing film to promote ballistic collisional mixing, metastable single phase face-centered-cubic Cu-rich and body-centered-cubic Cr-rich solid solutions have been grown on amorphous glass substrates at 75°C . The films were typically $1\ \mu\text{m}$ thick with average grain sizes of 90 and 110 nm, respectively, and a (111) preferred orientation. Annealing studies combined with x-ray and electron diffraction analyses showed that the films have good thermal stability against phase separation at temperatures up to 400°C . The metastable to equilibrium phase transformation occurred with the precipitation of an essentially pure second phase, rather than through a continuous series of metastable states, due to structural constraints.

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The Cu-Cr system exhibits a miscibility gap in the liquid phase and essentially no solid solubility at room temperature.¹ Even at the eutectic temperature, 1075°C , the solubility of Cr in fcc Cu is < 0.8 at. %. There is, however, a strong interest in producing metastable single phase Cu-Cr solid solutions, especially on the Cu-rich side where the addition of Cr would be expected to increase the corrosion resistance with the possibility of producing "stainless" Cu-based alloys.

Several investigators^{2,3} have shown that high energy, 100–300 keV, inert ion bombardment of thin film/substrate couples can lead to the formation of randomly mixed amorphous alloys through recoil implantation and cascade mixing processes. Such alloys can then transform to metastable crystalline phases upon subsequent annealing. However, Greene and coworkers^{4–7} have demonstrated that crystalline metastable phases can be formed directly by using low-energy (< 300 eV) inert ion bombardment of the growing film during deposition. Single crystal metastable alloys such as

$(\text{InSb})_{1-x}\text{Bi}_x$,⁴ $(\text{GaSb})_{1-x}\text{Ge}_x$,^{5,6} and $(\text{GaAs})_{1-x}\text{Ge}_x$,⁷ have been grown at elevated temperatures on single crystal GaAs substrates. These "ion-mixed" films do not require further post-deposition ion bombardment or annealing and exhibit good thermal and temporal stability.

This letter presents the initial results of an investigation into the growth and microstructure of metastable polycrystalline $\text{Cu}_{1-x}\text{Cr}_x$ solid solutions. Both fcc Cu-rich and bcc Cr-rich single phase alloys were grown on glass substrates using low-energy Ar^+ ion bombardment mixing during deposition. Films grown in the absence of ion bombardment were two-phase. The thermal stability of the ion-mixed single phase metastable alloys as well as the kinetics of the metastable to equilibrium phase transformation have been studied using x-ray and electron diffraction.

The films were grown by rf bias-sputter deposition. Two 10-cm-diam two-phase targets, one Cu-rich and one Cr-rich, were fabricated from 99.999% pure Cu and 99.9% pure Cr sheets. The Cu substrate plate was physically and