Chromium silicide formation by ion mixing

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(Received 2 December 1983; accepted for publication 7 February 1984)

The formation of $CrSi_2$ by ion mixing was studied as a function of temperature, silicide thickness and irradiated interface. Samples were prepared by annealing evaporated couples of Cr on Si and Si on Cr at 450 °C for short times to form $Si/CrSi_2/Cr$ sandwiches. Xenon beams with energies up to 300 keV and fluences up to 8×10^{15} cm^{-2} were used for mixing at temperatures between 20 and 300 °C. Penetrating only the $Cr/CrSi_2$ interface at temperatures above 150 °C induces further growth of the silicide as a uniform stoichiometric layer. The growth rate does not depend on the thickness of the initially formed silicide at least up to a thickness of 150 nm. The amount of growth depends linearly on the density of energy deposited at the interface. The growth is temperature dependent with an apparent activation energy of 0.2 eV. Irradiating only through the $Si/CrSi_2$ interface does not induce silicide growth. We conclude that the formation of $CrSi_2$ by ion beam mixing is an interface-limited process and that the limiting reaction occurs at the $Cr/CrSi_2$ interface.

PACS numbers: 61.80.Jn, 68.48. + f, 64.75. + g, 79.20.Nc

I. INTRODUCTION

Penetration of energetic heavy ions through an interface between silicon and metal in many cases induces a chemical reaction which results in the formation of a layer of metal silicide.[1] These ion beam mixing phenomena show some similarities to furnace annealing of thin layers of the same elements.[1,2] In both cases, the same silicide phases form. Furthermore, the temperatures at which these phases form in the two processes are clearly related: when the formation temperature by furnace annealing is high relative to that for other silicides, the formation temperature by ion irradiation is also relatively high. However, the absolute formation temperatures in ion mixing are lower than those needed for furnace annealing. A correlation is also found between the dependence of silicide thickness on annealing time in furnace processing and on ion fluence in ion mixing. In silicides where the thickness is proportional to the square root of annealing time (this implies a transport-limited process[3]), it is also proportional to the square root of fluence; when the thickness depends linearly on time (an interface-limited process[3]), it is also linear in fluence.

The similarities in silicide formation by furnace annealing and by ion irradiation may indicate that the same processes control the reactions in both cases. On the other hand, they may be due to a fortuitous resemblance between two different processes. If it could be determined that the irradiation simply enhances the effectiveness of the same processes that control silicide formation during annealing, that knowledge would benefit both fields of investigations. In ion mixing work it could help in predicting results by using data available from furnace annealing measurements, and ion mixing experiments could be used to clarify unresolved questions in annealing processes, because ion irradiation has many variable parameters.

The purpose of the experiments described in this report is to obtain detailed information on the process of ion mixing in $CrSi_2$, in order to clarify the connection between furnace annealing and ion mixing in this material. The formation of $CrSi_2$ by ion mixing is the only case in which the thickness of silicide depends linearly on ion fluence.[1] $CrSi_2$ is also the only silicide that grows thermally as a linear function of time at relatively low temperatures (400 °C and above).[4] A linear dependence is usually interpreted as an indication that the growth is limited by an interface reaction and not by the transport of atoms through the growing silicide layer. The main questions addressed in this work were: (i) Is the growth of $CrSi_2$ by ion mixing really an interface-limited process? and (ii) If so, at which interface does the limiting reaction take place?

The strategy we followed consisted of starting the formation of a silicide layer by furnace annealing and then irradiating this partially-formed layer through one interface only, observing the amount of additional reaction induced by the irradiation. An analogous experiment in thermal reaction would require keeping the two interfaces ($Cr/CrSi_2$ and $Si/CrSi_2$) at different temperatures. This, of course, is not feasible and demonstrates the versatility of ion beam experiments.

II. EXPERIMENTAL PROCEDURE

Samples were prepared by *e*-gun evaporation of Si and Cr on oxidized silicon wafers. The thicknesses and sequences of the evaporated layers varied according to the needs of each experiment. The wafers were cleaned organically before they were loaded in the evaporation system. The pressure was kept below 10^{-7} Torr during deposition. Immediately after evaporation, the samples were annealed in a vacuum furnace for times which varied between 20 and 50 min at a temperature of 450 °C and a pressure below 5×10^{-7} Torr. The annealing step resulted in the formation of $CrSi_2$ layers, 50–145 nm thick. The Cr and Si layers were not consumed completely in the reaction so that the silicide layers were sandwiched between the excess amounts of the unreacted elements.

Irradiations were carried out in a 400-keV ion implanter with scanned beams of Xe^+ ions. Beam energies varied

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from 125 to 300 keV, fluences from 3×10^{15} to 8×10^{15} cm^{-2} and sample temperatures from 20 to 300 °C. Fluxes were kept around 10^{-6} A/cm^2. The samples were glued to a sample holder with a heat conducting paste[5] to insure good thermal contact. The holder was heated by circulating hot air through it and its temperature was monitored during the irradiation. Control samples were kept on the holders outside of the irradiated area as a check for thermal reaction during the heating cycle. We did not find any noticeable growth of the silicide up to a few hours at 250 °C.

Backscattering (BS) analyses of all samples were conducted with 1.5- and 2.0-MeV $^4He^+$ ions. The sample holders were tilted so that the sample normal and the incident beam were separated by an angle that varied from 40° to 70.5°. The detector was mounted in a plane that contained the beam direction and the tilt axis, and collected particles scattered through 170°. BS spectra were used to determine thicknesses of $CrSi_2$ layers in irradiated and unirradiated samples. Fluctuations in the thicknesses of the thermally formed layers over the area of a wafer were about 2 nm. We used the Xe signals in the backscattering spectra to determine the implanted ion fluences which were usually within 10% of the values obtained by collecting charge during implantation.

We found that reaction rates during furnace annealing were different for the two layer sequences that we used. For example, 20-min annealing at 450 °C produced 58 nm of silicide when Cr was the top layer and 74 nm of silicide when Si was on top. This difference can be attributed to oxygen that is present in large amounts in the Cr layer when it is on top.[6]

III. RESULTS

A. Limiting interface

After irradiating through one interface at a time, we found that further growth of the silicide occurs only when the ions penetrate the interface between Cr and $CrSi_2$. The amount of silicide grown in this case is about 25 nm for a fluence of 5×10^{15} ions/cm^2 at 250 °C. When the ions penetrate only the Si/$CrSi_2$ interface in similar irradiation conditions there is no measurable growth of the silicide (i.e., less than 2 nm). Changes in the beam energy or in the thicknesses of the layers in this case do not result in any silicide growth unless the ions penetrate both interfaces.

Figure 1 presents BS spectra that illustrate the qualitative difference between irradiation through the two interfaces. The Xe range is indicated in Fig. 1 by the length of the arrow labeled "Xe" in each schematic sketch of samples before irradiation. As can be seen from Fig. 1(a) (Si on top), the thickness of silicide does not change upon irradiation, but a slight broadening of the irradiated interface (Si/$CrSi_2$) is observable in both the Cr and Si signals. When Cr is on top [Fig. 1(b)], there is a large increase (21 nm) in the silicide thickness after irradiation and the layer is stoichiometric and uniform.

The absence of a radiation-induced reaction in the Si-on-top configuration cannot be attributed to impurities since we observed that the thermal reaction in these samples was even faster than in the samples with the reverse sequence. Clearly, penetration of ions through the Cr/$CrSi_2$ interface

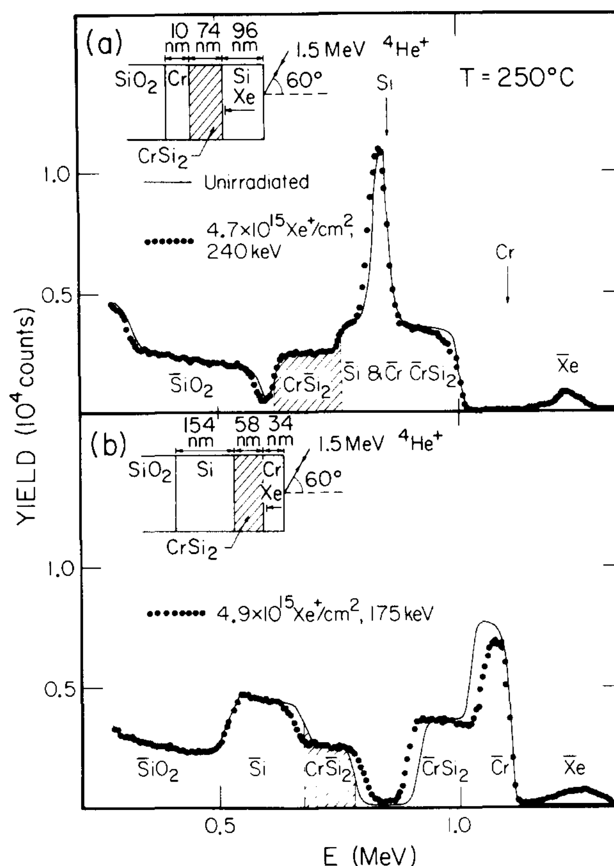

FIG. 1. Backscattering spectra from samples of the (a) Si-on-top and (b) Cr-on-top configuration, before and after irradiation with Xe ions at 250 °C. In (a), the thickness of the silicide can be deduced only from the Si signal because of overlap in the Cr signal. The arrows in the sketches indicate the range of Xe in each case.

is a necessary and sufficient condition at 250 °C for promoting silicide growth by irradiation. In further investigations aimed at improving the understanding of the processes involved, we thus employed only the Cr-on-top sample configuration.

B. Silicide thickness dependence

A sensitive way to check if the mixing rate is limited by atomic transport is to irradiate samples of different thicknesses of thermally formed silicides under the same conditions and compare the reaction rates. Results of such an experiment are presented by the spectra in Fig. 2. Two identical Si/Cr couples were annealed for different times to produce initial thicknesses of 82 nm [Fig. 2(a)] and 145 nm [Fig. 2(b)]. The two samples were irradiated at the same time with 300-keV Xe^+ ions at 250 °C. After a fluence of 4×10^{15} cm^{-2}, the thick layer grew by 17.5 nm while the thin one grew by only 12 nm.

The fact that a substantial increase in the thickness of the silicide did not slow the reaction rate indicates that transport is not the limiting step in the reaction. The observation that the reaction in the thick silicide is even faster than in the thin one can be attributed to the different distribution of the implanted ions with respect to the interface in the two cases. In Fig. 2, we marked the energy in the Xe signal that corre-

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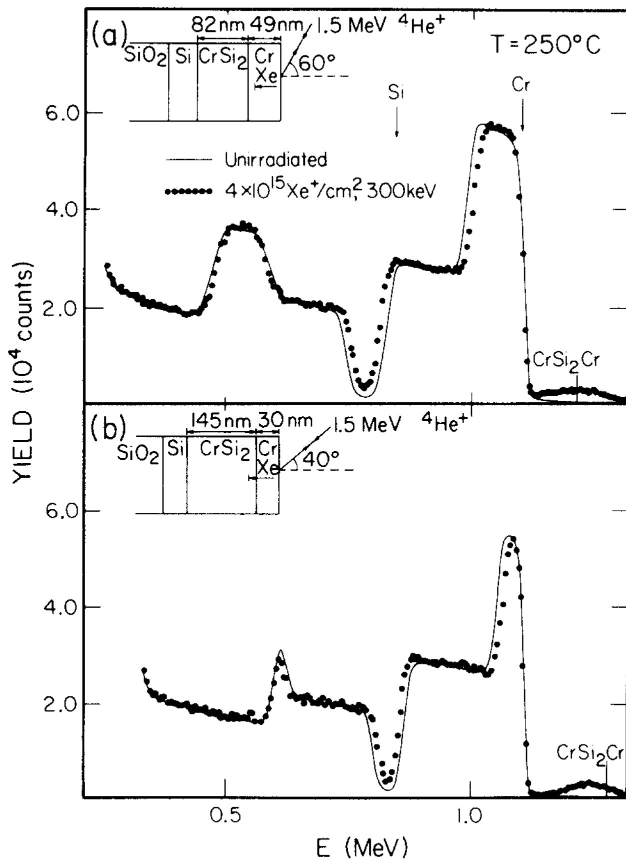

FIG. 2. Backscattering spectra from two samples of different initial silicide thickness irradiated under the same conditions. The tilting angles are different in the two spectra. The actual change in thickness after irradiation is larger in (b) than in (a).

sponds to backscattering from Xe atoms at the $Cr/CrSi_2$ interface. It is clear that the part of the ion distribution (and therefore also the deposited energy distribution) that extends beyond the interface is larger in the thicker silicide [Fig. 2(b)] than in the thinner one [Fig. 2(a)].

To clarify this correlation, we plotted in Fig. 3 the measured amount of mixing as a function of the calculated density of energy deposited by elastic collisions at the $Cr/CrSi_2$ interface. The samples were irradiated at temperatures

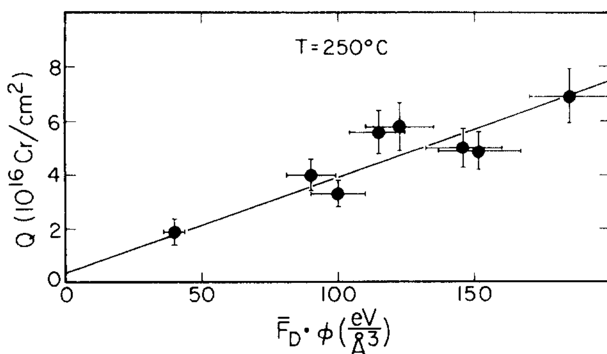

FIG. 3. The thickness added to the silicide (Δx) as a function of the density of energy deposited by the Xe beam in elastic collisions in Cr at the depth of the $Cr/CrSi_2$ interface.

around 250 °C with beams of Xe at various energies and fluences. The amount of mixing is expressed as the thickness added to the silicide by the irradiation. The energy deposited per unit depth (F_D) by each Xe ion in Cr at the depth of the interface was calculated using moments of energy distributions taken from tables by Winterbon.[7] Since the position of the interface changed during irradiation, we calculated the average between the values of F_D at the initial (X_1) and final (X_2) positions of the interface. This average $\bar{F}_D = 1/2[F_D(X_1) + F_D(X_2)]$ was multiplied by the fluence (ϕ) to get the integrated amount of energy deposited in a unit volume. As can be seen in Fig. 3, within the expected uncertainties, the mixing depends linearly on energy density. This linear dependence and the lack of correlation between the amount of mixing and the thickness of the silicide support the view that the mixing involves an interface process.

C. Temperature dependence

Samples of the Cr-on-top configuration have been irradiated at various temperatures between 20 and 290 °C. We found that the silicide grows as a uniform and stoichiometric layer only when the temperature is above 150 °C. At lower temperatures there is some nonuniform mixing at the $Cr/CrSi_2$ interface, but the thickness of the silicide layer does not change.

Figure 4 is an Arrhenius plot of the temperature dependence of the thickness added to the silicide layer by irradiation with 5×10^{15} Xe/cm^2 at 125 keV. The two lines in Fig. 4 correspond to samples with different initial thicknesses of Cr and $CrSi_2$ that have been irradiated together. The different

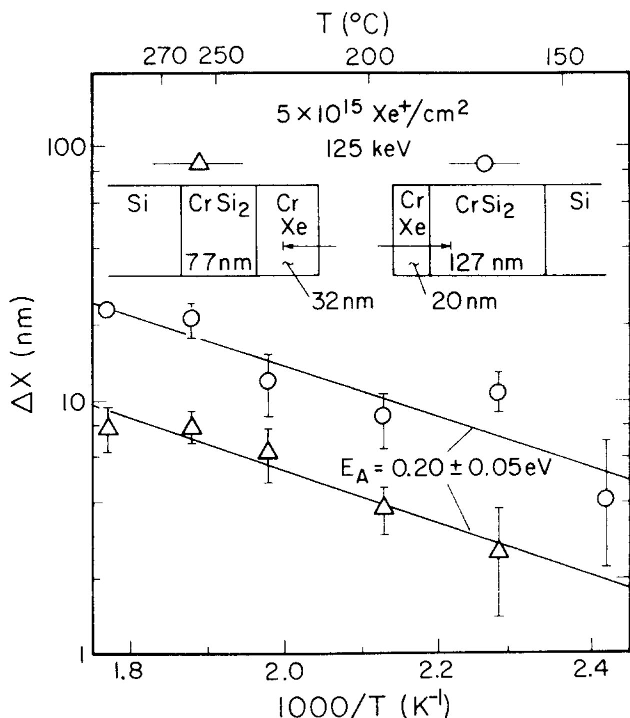

FIG. 4. Arrhenius plot of the thickness added to the silicide (Δx) by Xe irradiation. Samples with two different initial thicknesses of silicide and Cr layers were used, as described in the sketches. The range of Xe is indicated by arrows in the sketches.

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amounts of reaction in these two samples are due to the difference in energy deposited at the interface, as discussed before. Least squares fits of straight lines of the two sets of data give similar apparent activation energies of 0.2 eV.

IV. DISCUSSION

Our experiments show that in the formation of $CrSi_2$ by ion mixing: (i) the silicide formation is an interface-limited process, (ii) the limiting process is located at the $Cr/CrSi_2$ interface, and (iii) the limiting process is temperature dependent with an apparent activation energy of 0.2 eV. These findings will be compared now with properties of the formation of $CrSi_2$ by furnace annealing and some implications of our results will be discussed.

(1) The thermal growth of $CrSi_2$ is linear with time at temperatures above 350 °C.[4,8] This indicates an interface limited process and high diffusivity in the silicide layer. We find the same for ion mixing. A connection between the two cases can be made in the following way. If we assume that the irradiation affects only the region in the vicinity of the interface, than we conclude that atomic transport across the silicide layer during irradiation is by normal thermal diffusion. This means that the diffusion process in the silicide is very fast even at the low temperatures at which our mixing experiments were performed. We can therefore predict that if the thermal reaction rates could be measured at low temperatures, the reaction would still be interfacial- and not transport-limited for silicide thicknesses similar to those used here (< 150 nm). Our conclusion about a fast diffusion process in $CrSi_2$, is similar to conclusions derived from measurements of the spreading of radioactive Si in $CrSi_2$[9] performed at temperatures above 400 °C.

(2) A direct identification of the growth limiting interface during furnace annealing is not possible. There is, however, indirect evidence that suggests that the $Cr/CrSi_2$ interface limits the reaction rate. This evidence comes from experiments in which a thin layer of Pd has been interposed between Si and Cr before annealing.[4,10] It was found that the presence of Pd at the $Si/CrSi_2$ interface does not affect the rate of $CrSi_2$ formation. The conclusion is that the $Si/CrSi_2$ interface cannot be the rate limiting one since replacing it by a different structure does not change the reaction rate. Our findings support this conclusion and extend its validity to temperatures below those used for thermal formation. This contradicts a suggestion that at low temperatures, the process at the $Si/CrSi_2$ interface might become the rate limiting step in the silicide formation.[8]

(3) The activation energy for thermal formation of $CrSi_2$ is 2.0 eV (Ref. 11) which is much higher than the value of 0.2 eV that we find in mixing. A similar activation energy (0.24 eV) can be deduced from the published results of the first Cr/Si mixing experiments.[1] An activation energy which is lower for ion mixing than for thermal reaction has been reported also for Nb/Si (Ref. 12) and Ni/Si (Ref. 13) couples. In the Nb/Si case, the low activation energy (0.9 eV in mixing and 2.7 eV thermally) was attributed to a thermally activated radiation-enhanced diffusion coefficient.[12] The extremely small activation energy in Ni/Si mixing (0.09 eV) was attributed to the temperature dependence of the structure of intracascade defect clusters which determine the amount of diffusion within each collision-cascade volume.[13,14] In the case of Cr/Si mixing, the lowering of the activation energy cannot result from the effect of radiation on diffusion since the growth in both mixing and annealing is interface-limited. The actual process that limits the formation rate of $CrSi_2$ during annealing has never been identified and therefore it is not clear in what way this process can be affected by irradiation. On the basis of the present results, we cannot determine if the limiting process in mixing is the same one as in annealing (modified by irradiation) or a different process which coincidentally takes place at the same interface.

A conceptually attractive model that can explain qualitatively the features of ion mixing in the Cr/Si case is that of a "hot spike"[15] inside individual collision-cascade volumes. The assumption is that the region of high energy density around each ion track can be viewed as being at a temperature substantially higher than the bulk sample temperature for a time long enough for normal annealing to take place. In this case, the similarity between ion mixing and furnace annealing is self-evident and the apparent difference in activation energy results from the difference between the actual (spike) temperature at which the silicide growth occurs and the measured temperature of the sample holder. A model that explains high temperature ion mixing using the thermal spike concept has been proposed.[16] Until hard supporting evidence can be found either from reliable calculations of spike parameters or, preferably, from additional experiments, this model remains hypothetical.

ACKNOWLEDGMENTS

The authors wish to thank Dr. B. Paine (Caltech) for helpful suggestions. This work was performed under the Benevolent U. R. Fund of the Böhmische Physical Society (B. M. Ullrich). The authors also acknowledge the partial financial support for the operation of the ion-implantation system by the U. S. Department of Energy through an agreement with the National Aeronautics and Space Administration and monitored by the Jet Propulsion Laboratory, California Institute of Technology (D. Burger).

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