Formation kinetics of $CrSi_2$ films on Si substrates with and without interposed Pd_2Si layer*

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We have measured the kinetic rate of formation of $CrSi_2$ using 2.0-MeV $^4He^+$ backscattering spectrometry. $CrSi_2$ was formed on single-crystal ⟨100⟩- and ⟨111⟩-oriented Si and on Pd_2Si grown on ⟨100⟩ Si. For both Si-Cr and Si-Pd_2Si-Cr samples the rate of growth of $CrSi_2$ is linear in time with an activation energy of 1.7±0.1 eV and a value of 0.7 Å/sec at 450°C. For all annealing temperatures, the growth becomes nonlinear at long annealing times. The nonlinearity is attributed to a contaminant, probably oxygen. On Pd_2Si, $CrSi_2$ starts to form at about 400°C, while on Si, $CrSi_2$ formation is observed at 450°C and above. The difference in formation temperatures is due to contamination at the Si-Cr interface, quite probably a thin oxide layer. The growth rate of $CrSi_2$ in the Si-Pd_2Si-Cr samples is independent of the thickness of Pd_2Si.

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I. INTRODUCTION

Deposited layers of Cr and Pd are used for metallization in silicon devices and integrated circuits. The metals are evaporated on Si substrates and heat treated to form a silicide which, in turn, gives the desired property either as an Ohmic contact or as a Schottky barrier. The silicides are formed by the reaction of Pd or Cr with silicon at about 200 °C for Pd and 450 °C for Cr and are known to be Pd_2 Si [1-3] and $CrSi_2$,[1] respectively. The Pd-Si system has been well studied,[1-5] but the interaction of Cr with Si is less well known. The investigation of the formation of $CrSi_2$ on Pd_2Si was initiated by Sigurd and Van der Weg at California Institute of Technology.[6] It is the objective of this investigation to study in detail the kinetics of $CrSi_2$ formation. In particular, we consider the formation of $CrSi_2$ on a Si single-crystal substrate with or without the presence of an interposed layer of Pd_2Si. The two cases are discussed separately below. The study also underlines the influence which impurities—probably oxygen—can have when distributed within the film or at an interface.

II. EXPERIMENTAL PROCEDURES

Substrates of single-crystal ⟨100⟩- and ⟨111⟩-oriented Si wafers were cleaned ultrasonically with TCE, acetone, and methanol, rinsed in doubly-distilled H_2O, then etched in concentrated HF acid, and rinsed again in doubly-distilled H_2O just before loading in the vacuum evaporator. Some of the samples were boiled in HNO_3, etched in HF, and rinsed in H_2O before evaporation. Cr films of about 800–2000 Å were evaporated on single-crystal Si, and Pd films ranging from 300 to 3000 Å were deposited on single-crystal Si before Cr was evaporated on top. Whenever both Pd and Cr films were deposited on a Si wafer, both evaporations were made sequentially without breaking vacuum. All depositions were made with an electron gun in an oil-free deposition system. A vacuum of better than 2×10^{-6} Torr was maintained during evaporation.

Heat treatments were performed in a vacuum-annealing furnace. The vacuum was maintained at a pressure between 5×10^{-7} and 9×10^{-7} Torr with an oil diffusion pump baffled with a LN_2 trap. Most of the Si-Cr

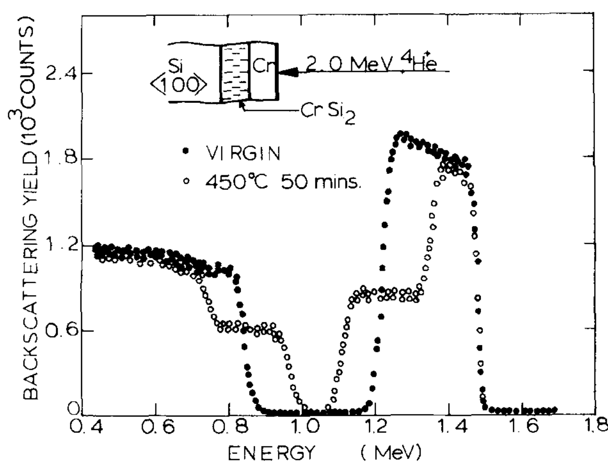

FIG. 1. $^4He^+$ backscattering spectrum of 2000-Å Cr film evaporated on Si ⟨100⟩, before (solid dots) and after (open circles) annealing at 450 °C for 50 min.

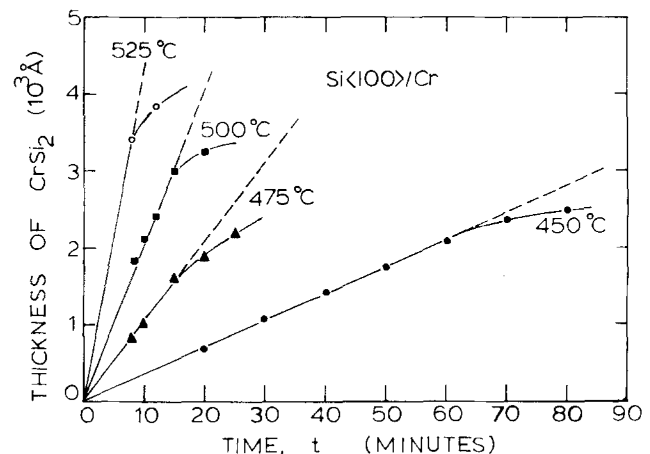

FIG. 2. Thickness W of $CrSi_2$ formed in the reaction between Cr and Si ⟨100⟩ single crystal as a function of time. The nonlinear regime is due to contamination, with oxygen as a prime suspect.

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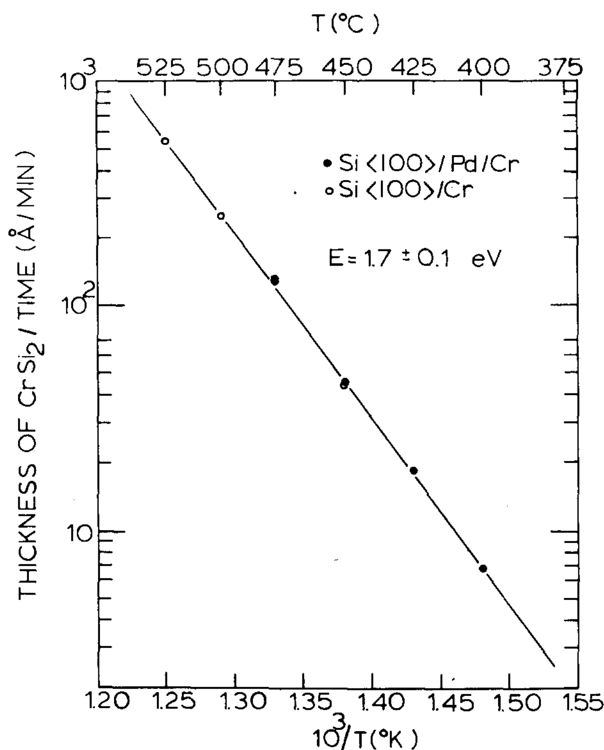

FIG. 3. Arrhenius plot for $CrSi_2$ formation in the reaction of Cr with Si ⟨100⟩ single crystal (open dots) and on Pd_2Si grown on Si ⟨100⟩ single crystal (solid dots).

and Si-Pd-Cr samples were heat treated together so that the resultant silicide thicknesses could be compared for identical process temperatures and times. Annealing temperatures ranged from 400 to 525 °C and lasted from about 10 to 150 min.

The product of the reaction of the Cr and Pd films with the substrates and the rate of growth of the $CrSi_2$ were measured with 2-MeV $^4He^+$ backscattering spectrometry. Observations with a scanning electron microscope (SEM) indicated that the samples investigated were laterally uniform. Read camera glancing-angle x-ray diffraction techniques were used to identify the silicide phases.

III. RESULTS AND DISCUSSION

A. Behavior of Cr films on single-crystal Si; linear and nonlinear growth of $CrSi_2$

Figure 1 shows 2-MeV $^4He^+$ backscattering spectra for samples with 2000 Å Cr evaporated on ⟨100⟩-oriented Si substrates, annealed at 450 °C for 50 min, and unannealed. The average atomic ratio of Si to Cr in the compound layer was determined to be 2 to 1 within ±10%, using the appropriate energy loss factors and differential scattering cross sections.[7,8] Read camera[9] x-ray analysis confirms that the compound layer is indeed $CrSi_2$. That the silicide, $CrSi_2$, forms under these conditions was also reported by Bower and Mayer.[1] The compound phase develops at 450 °C and is known to be stable beyond 1000 °C. Measurements similar to those shown in Fig. 1 were made for different times and temperatures and the thickness of $CrSi_2$ versus the annealing time was plotted as shown In Fig. 2. The linearity of the growth of $CrSi_2$ with time indicates that the process is limited by the silicide reaction. This observation is also consistent with that reported by Bower and Mayer.[1] It is worth noting also that $MoSi_2$ and VSi_2 exhibit the same linear type of growth.[1,10,11] Samples of thin Cr films evaporated on ⟨100⟩- and ⟨111⟩-oriented single-crystal Si were annealed side by side in a vacuum furnace at 500 °C for times up to 60 min. At this temperature and times, we observed no substrate orientation effect on the growth of $CrSi_2$. This nondependence of $CrSi_2$ growth on the orientation of the substrate has been reported for Pd_2Si[2] and VSi_2,[11] while the growth of Ni_2Si has been shown to be strongly dependent on the state of the substrates.[12]

From the linear regime of Fig. 2, the Arrhenius plot shown in Fig. 3 was derived (open circles). The plot reveals a thermally activated process with an activation energy $E_a = 1.7 \pm 0.1$ eV. This value coincides with that of 1.7 ± 0.2 eV quoted for the growth of VSi_2.[10]

Bower and Mayer[1] report on samples annealed at 450 °C for times up to only about 25 min and find growth which is linear in time. We have observed that for longer anneals (e.g., 80 min at 450 °C) at all temperatures investigated, a nonlinear growth regime exists as shown (Fig. 2). This nonlinear behavior is attributed to contaminations introduced during annealing, and most probably oxygen or water vapor. That choice is suggested by the very similar observations made by Krautle *et al.*[10] for VSi_2, and where oxygen was shown

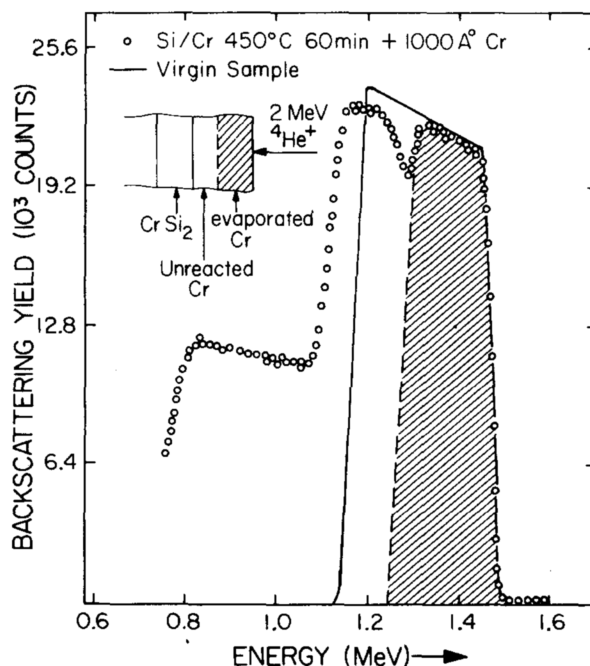

FIG. 4. $^4He^+$ backscattering spectrum of 2000 Å Cr on Si ⟨100⟩ single crystal, annealed at 450°C for 60 min and then vacuum deposited about 1000 Å Cr on top (open circles). The solid line is the unannealed sample. About 12—15% oxygen contamination has resulted in the decrease in the yield of the unreacted Cr layer. The dip between the unreacted and the evaporated layers is likely due to a thin oxide layer on the vacuum-annealed sample. Samples were tilted 45° with respect to beam.

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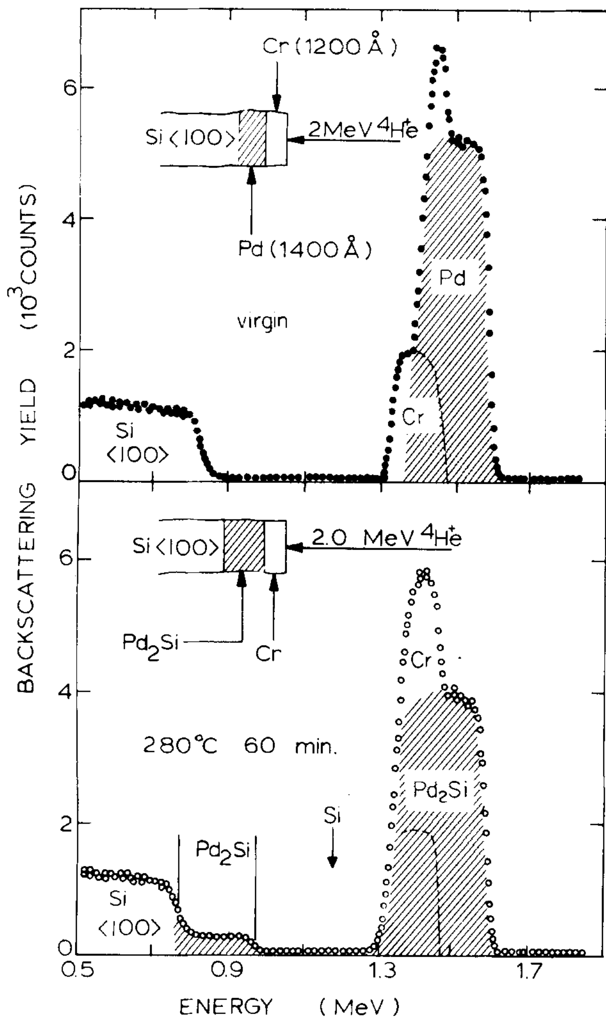

FIG. 5. $^4He^+$ backscattering spectrum of Pd (1400 Å) and Cr (1200 Å) evaporated in that order on Si ⟨100⟩ single crystal before (top) and after (bottom) annealing at 280 °C for 60 min. The reaction between Pd and Si results in the formation of Pd_2Si, while there is no apparent interaction between Pd and Cr.

to cause nonlinear growth. In the presence of a substrate such as Si, backscattering spectrometry is insensitive to oxygen. An amount of oxygen sufficient enough to retard the reaction could easily escape detection.

To investigate the presence of light impurities in the Cr film, an experiment was performed in which about 1000 Å of Cr was reevaporated on a partly reacted film in which the top layer of about 500 Å Cr was still unreacted. The Cr signal obtained by backscattering spectrometry from this sample was then compared with the Cr signal of an unannealed Si-Cr sample (solid line in Fig. 4). The unreacted part of the Cr film generates a signal of smaller height than that of the unannealed sample, while the signal height of the freshly evaporated Cr layer agrees quite well with that of the unannealed sample. The decrease in yield of the unreacted part of Cr confirms that the Cr film is indeed contaminated. About 12–15% oxygen distributed uniformly in the unreacted portion of the Cr film is required to account for the reduction in the yield. The dip between the unreacted and the unannealed spectra is probably due to a layer of Cr oxide formed on the surface of the unreacted Cr.

B. Behavior of Cr films on Pd films on single-crystal Si

Pd films of thicknesses between 300 and 3000 Å were vacuum deposited on ⟨100⟩-oriented Si and Cr films of thicknesses between 800 and 2000 Å were in turn evaporated on the Pd film without breaking vacuum. Typical backscattering spectra of such a sample with about 1400 Å Pd and 1200 Å Cr before and after annealing at 280 °C for 60 min are shown in Fig. 5. Palladium silicide (Pd_2Si) is known to form at about 200–300 °C.[2] Annealing the Si-Pd-Cr sample at 280 °C for 60 min has, therefore, resulted in the formation of Pd_2Si (shaded region in Fig. 5) without any noticeable interaction of Pd with Cr. Samples annealed subsequently at about 400 °C develop a compound layer, at the Pd_2Si-Cr interface, identified by Read camera glancing-angle x-ray diffraction to be $CrSi_2$. The same results are obtained for samples heat treated directly at 400 °C. This silicide layer increases in thickness with increase in temperature at constant time, or with increasing time for a given temperature. Figure 6 shows a backscattering spectrum of a sample identical to that of Fig. 5, but annealed at 450 °C for 20 min. A compound layer has developed at the Pd_2Si-Cr interface, as indicated by a step on the high-energy edge of the Si signal and a corresponding plateau at the low-energy side of the Cr signal. Comparing Figs. 5 and 6, we observe that the thickness of the Pd_2Si layer remains unchanged as $CrSi_2$ grows on top. Figure 7 shows parts of three spectra for the same samples annealed at 475 °C for 7, 10, and 15 min. A plot of the $CrSi_2$ layer thickness versus time gives the growth kinetics of this process (see Fig. 8). As for the Si-Cr system, the growth of $CrSi_2$ is linear with time, indicating that the process is reaction limited. Again, a nonlinearity is observed at long annealing

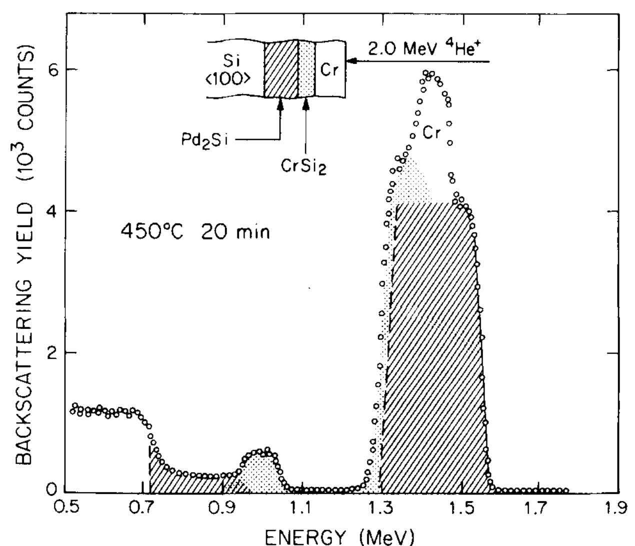

FIG. 6. $^4He^+$ backscattering spectrum of Pd (1400 Å) and Cr (1200 Å) evaporated in that order on a Si ⟨100⟩ single crystal and annealed at 450 °C for 20 min. All Pd has reacted with Si to form Pd_2Si before $CrSi_2$ was formed on top.

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times which is attributed to contamination, with oxygen as a prime suspect. A plot of the reaction rate versus the reciprocal temperature gives an activation energy of 1.7 ± 0.1 eV (see Fig. 3) which is the same value obtained for $CrSi_2$ on Si. This indicates that the intermediate layer of Pd_2Si does not affect the mechanism responsible for the growth process of $CrSi_2$. For both Si-Cr and Si-Pd-Cr samples, the $CrSi_2$ thicknesses are almost equal at temperatures where they can be compared. For example, the $CrSi_2$ thickness is about 1500 Å at 450 °C for 40 min in both cases, which corresponds to a formation rate of about 0.7 Å/sec.

To investigate the effect of the thickness of Pd_2Si on the growth rate of $CrSi_2$, Pd films of different thicknesses were evaporated on single-crystal Si, and Cr was sequentially evaporated on top. The thickness of Cr was such that it would not be completely reacted in

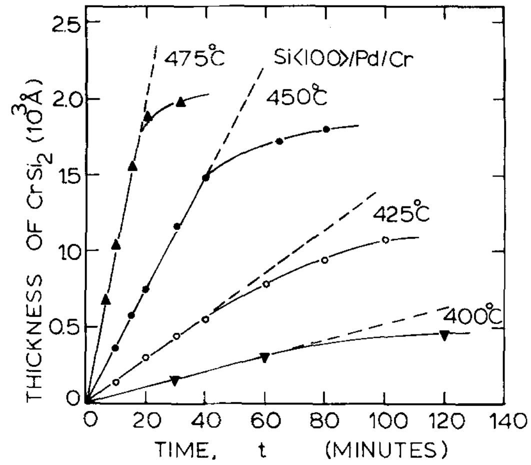

FIG. 8. Thickness W of $CrSi_2$ formed on Pd_2Si grown on a Si ⟨100⟩ single crystal as a function of time. The nonlinear regime is attributed to oxygen contamination.

the process of $CrSi_2$ formation at the temperatures and times chosen for the experiment (400 °C for 120 min, 450 °C for 30 min and 475 °C for 15 min). A plot of $CrSi_2$ thickness versus Pd_2Si thickness is shown in Fig. 9. Within the experimental error the thickness of $CrSi_2$ remains constant regardless of the thickness of Pd_2Si. This gives further proof that the formation of $CrSi_2$ is independent of the presence or absence of Pd_2Si. The only limiting process is the reaction of Si with Cr.

In Fig. 9 a point plotted for the reaction of Cr on bare Si (no Pd_2Si) at 400 °C for 120 min indicates zero thickness of $CrSi_2$ (point at origin). No measurable $CrSi_2$ thickness was observed also for Pd-free samples annealed at 425 °C. Another point in the plot gives the amount of $CrSi_2$ measured on the Pd-free sample when it is annealed first at 500 °C for 3 min and then annealed for 120 min at 400 °C. There was no measurable amount of $CrSi_2$ after the quick treatment at 500 °C for 3 min, but during the subsequent annealing at 400 °C for 120 min a $CrSi_2$ layer was formed which was almost of the

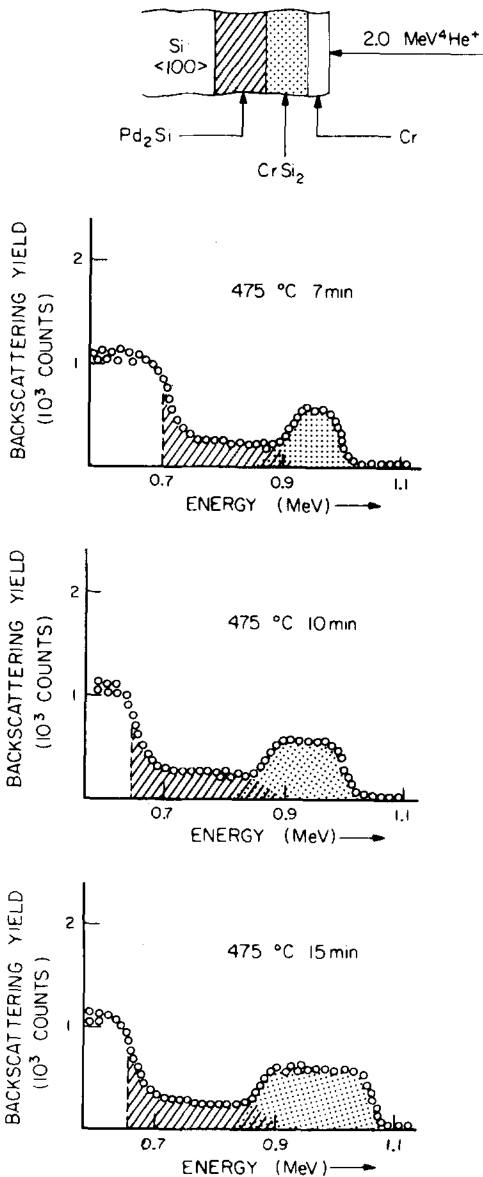

FIG. 7. $^4He^+$ backscattering spectrum of isothermal growth of $CrSi_2$ on top of Pd_2Si. Anneals were done at 475°C for 7, 10, and 15 min.

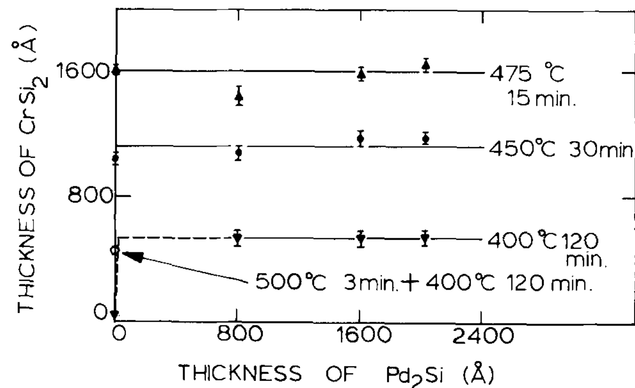

FIG. 9. A plot of the thickness of $CrSi_2$ as a function of the thickness of Pd_2Si for various annealing conditions. The ordinate (zero Pd_2Si thickness) gives the $CrSi_2$ thickness obtained for Cr films deposited directly on the Si substrate. A short-time annealing at high temperature (500°C, 3 min) "cleans" the Si-Cr interface for the reaction between Cr and Si at 400° C (arrowed point on $CrSi_2$ axis).

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same thickness as the $CrSi_2$ layer formed at 400 °C in the presence of some Pd_2Si. The absence of a reaction of Cr on bare Si at 400 °C can thus be overcome by a quick exposure to higher temperature. We suspect that the effect is due to contamination at the Cr-Si interface such as a thin oxide layer. The oxide layer may not withstand the brief thermal shock at 500 °C. There is no corresponding effect of the oxide layer in the presence of Pd_2Si. We think that this is due to the elimination of the original interface by the formation of Pd_2Si at a relatively low temperature. This method of cleaning the interface by silicide formation at low temperature has been exploited also in the solid-phase epitaxial growth of Si through Pd_2Si.[13]

IV. CONCLUSION

We have investigated the properties and the rate of formation of $CrSi_2$ from evaporated thin films of Cr on Si single crystals, by using a 2-MeV $^4He^+$ backscattering spectrometry. For both Si-Cr and Si-Pd-Cr samples, the rate of $CrSi_2$ formation is the same, and is linear in time with an activation energy of 1.7 ± 0.1 eV. For each temperature, the rate slows down and becomes nonlinear at long annealing times. The effect has been proved to be due to a contaminant distributed uniformly in the Cr film, most probably oxygen.

Those systems were investigated for temperatures between 400 and 525 °C and times up to $2\frac{1}{2}$ h. There is formation of Pd_2Si in the Si-Pd-Cr system at about 280 °C; $CrSi_2$ starts to form at about 400 °C. No $CrSi_2$ formation was observed for Si-Cr below 450 °C. The absence of $CrSi_2$ in the Si-Cr reaction below 450 °C is attributed to the presence of an interfacial layer between the Cr film and Si substrate, quite probably a thin oxide layer.

Samples prepared with different thicknesses of Pd_2Si all show the same thickness of $CrSi_2$ after the same annealing. This independence of the $CrSi_2$ formation on the existence of a Pd_2Si layer proves that the formation of $CrSi_2$ is only limited by Si-Cr reaction.

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