Kinetics of $TiSi_2$ formation by thin Ti films on Si

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(Received 28 March 1983; accepted for publication 12 May 1983)

Silicide formation with Ti deposited on single crystal Si and Ti deposited on amorphous Si layers sequentially without breaking the vacuum was investigated using backscattering spectrometry and glancing-angle x-ray diffraction. For Ti deposited on amorphous Si, $TiSi_2$ was formed with a rate proportional to $(\text{time})^{1/2}$ and an activation energy of 1.8 ± 0.1 eV. For Ti deposited on single crystal Si, the reaction rate was slower and the silicide layer was nonuniform in thickness. We attribute the difference in behavior to the presences of interfacial impurities in the case where Ti was deposited on single crystal Si.

PACS numbers: 68.48. + f, 64.70.Kb, 61.70.Tm, 82.65.Jv

I. INTRODUCTION

The formation of silicides by solid-phase reaction of thin metal films deposited on single-crystal silicon substrates upon steady-state or transient annealing has been the object of intense investigation.[1] Interest in this subject is spurred by the great practical significance of forming reproducibly reliable metal contacts to silicon devices.

Among the silicide-forming metals, Ti has special significance. Titanium is much used as a first layer in metallization systems because of its good adhesion to both Si and SiO_2. It is well known that upon thermal annealing in vacuum, Ti films deposited on Si substrates transform to $TiSi_2$ at temperatures above about 600 °C.[2–5] The kinetics of that reaction has never been reported in detail, the reason being that the results on the kinetics of that reaction were not reproducible, while the phase formed ($TiSi_2$) almost always was. This state of affairs is typical for most early transition metals, as is exemplified by the results for V,[6–8] Nb,[8] and Mo.[9] The early results of detailed studies on V[7,8] and Nb[8] have shown that the kinetics can be altered significantly by interfacial impurities or residual gas in the annealing ambient. More recently, Murarka and Fraser[5] have studied the silicide formation of sputtered Ti films and concluded that TiSi forms first with such films, at temperatures around 600 °C and that TiSi then transforms into $TiSi_2$. For vacuum deposited films of Ti, the first phase observed has consistently been reported to be $TiSi_2$. Since sputtered layers always contain impurities, such as the sputtering gas itself, these results suggest that impurities are important in the determination of the first growing phase as well.

The results of the present investigation show that reproducible kinetics for the growth of $TiSi_2$ by thermal annealing at temperatures between 475 and 550 °C in a vacuum of evaporated Ti films can be obtained if the Si/Ti couple is deposited in a dry vacuum by consecutive evaporation of the two elemental films without breaking the vacuum. To our knowledge, this represents the first reproducible measurement of $TiSi_2$ reaction kinetics.

II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURES

Silicon substrates, ⟨100⟩ in orientation, were organically cleaned and etched in dilute HF immediately prior to loading in an oil-free vacuum system. Thin Ti layers were electron-gun deposited onto these substrates, followed immediately by an evaporation of an amorphous Si[Si(*a*)] layer without breaking the vacuum. The vacuum during deposition was better than 5×10^{-7} Torr. The deposition rates were 20 Å/sec for Ti and 50 Å/sec for Si. In some cases, an Si(*a*) layer was deposited on a SiO_2 substrate cleaned in organic solvents followed by the deposition of a Ti layer, again without breaking the vacuum. The Ti–Si(*a*) interface of these bilayers is believed to be fairly clean. At times, the Si(*a*) was purposely contaminated by exposing the Si(*a*) layer to air for several days, then cleaning it by the identical procedure used for the ⟨100⟩Si[Si(*xtl*)] substrates, and depositing the Ti on top.

The samples were annealed in an oil-pumped vacuum furnace at $\sim5\times10^{-7}$ Torr, with varying temperatures and times. To limit interference by residual gases in the vacuum, a piece of sapphire previously cleaned by organic solvents was placed on the sample during annealing.

MeV $^4He^+$ backscattering spectrometry and x-ray diffraction were used to investigate the samples and establish the growth kinetics of the interfacial layer formed during vacuum annealing.

III. RESULTS

The same thin Ti film reacts differently with Si(*a*) and with Si(*xtl*). A direct demonstration of that fact is offered by the results of Fig. 1, which shows backscattering spectra of a Ti layer sandwiched between a Si(*xtl*) substrate and a Si(*a*) overlayer. Annealing for 13 min at 525 °C results in the formation of a $TiSi_2$ layer between Ti and Si(*a*) while no reaction can be detected between Ti and Si(*xtl*). After 39 min of an-

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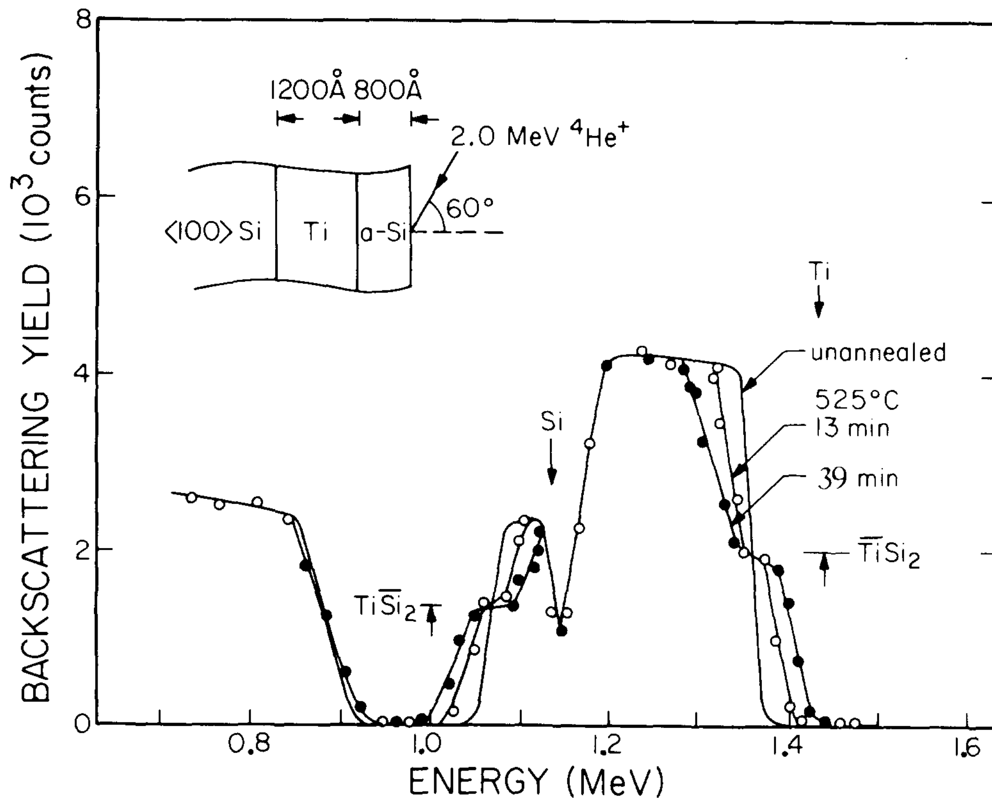

FIG. 1. 2.0-MeV $^4He^+$ backscattering spectra showing that an evaporated Ti film reacts faster with the Si(*a*) layers than with the ⟨100⟩ Si substrates. The samples were prepared by consecutive evaporation of Si and Ti films on the ⟨100⟩ Si substrates without breaking the vacuum.

nealing, a faint indication of a reaction is seen between Ti and Si(*xtl*); with Si(*a*) a continued growth of the $TiSi_2$ layer is observed. Clearly, the Ti film reacts faster with the Si(*a*) layer than with the Si(*xtl*) substrate.

To investigate the difference in the two reactions, a Ti film was deposited simultaneously on a Si(*a*) [Fig. 2(a)] and a Si(*xtl*) [Fig. 2(b)] wafer substrate. Different pieces of each of these two wafers were then annealed simultaneously at different times and temperatures. The thickness of the interfacial layer formed during annealing was measured by backscattering spectrometry (see Fig. 2). The atomic composition of the formed layer corresponds to $TiSi_2$ in all cases, and x-ray diffraction measurements on samples with the thickest interfacial layer confirmed the presence of this phase. However, the temperatures at which a noticeable reaction sets in are higher for Ti/Si(*xtl*) bilayers than for Ti/Si(*a*) samples and the interface of silicide and Si substrate is less abrupt in the first case.

Figure 3 gives the $TiSi_2$ layer thickness versus square root of annealing time for the Ti/Si(*a*) case. The data fit a linear dependence with $(\text{time})^{1/2}$ which indicates a diffusion-limited reaction. The activation energy of the process is about 1.8 ± 0.1 eV, as shown in Fig. 4.

The reaction rates of Ti films with Si(*a*) is reproducible; i.e., samples prepared at different times yield the same rates. For example, the $TiSi_2$ film thicknesses derived from the spectra of Fig. 1 are plotted in Fig. 3 as well (square dots, for 525 °C). The rate derived for that sample (dashed line) agrees closely with the rate of the sample used in Fig. 2(a).

In contrast to the reproducible results obtained from the Ti/Si(*a*) samples, when the Ti/Si(*xtl*) sample was cut into several pieces and annealed simultaneously, a variation in thickness of $TiSi_2$ formed thermally was found. These results

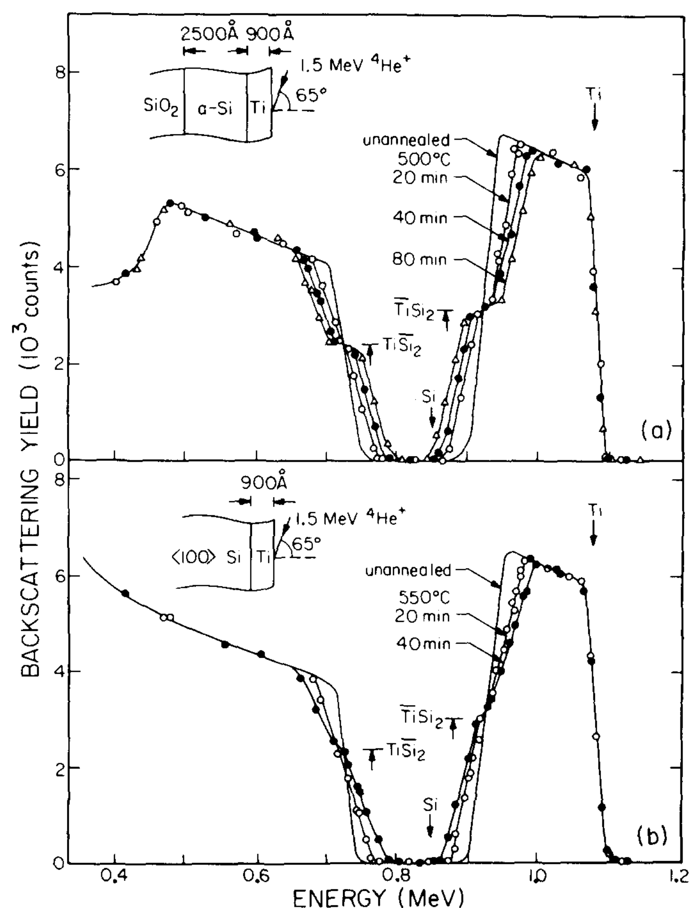

FIG. 2. 1.5-MeV $^4He^+$ backscattering spectra after annealing of Ti/Si bilayers obtained by vacuum evaporation of a Ti layer (a) on Si(*a*) deposited on SiO_2 just prior to the Ti films without breaking the vacuum; (b) on ⟨100⟩ Si substrates.

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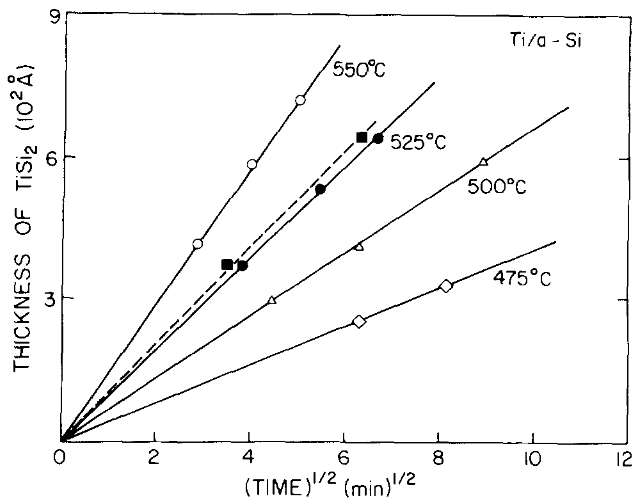

FIG. 3. Thickness of $TiSi_2$ vs square root of annealing time for the Ti/Si(a) samples of Fig. 2(a). The $TiSi_2$ film thicknesses derived from the spectra of Fig. 1 are plotted as well (square dots and dashed line).

also show that the reaction kinetics are not due to the incursion of oxygen during annealing.

In this work the formation of $TiSi_2$ for the Ti deposited on Si with a relatively clean interface can be observed at 475 °C, a temperature which is much lower than the values reported in the previous investigations (~600 °C). We thus reduced the annealing temperature to 450 °C to determine if a reaction threshold can be found. Instead of a threshold, we found at that low temperature the reaction begins with the formation of a thin (~200 Å) layer of TiSi, which later disappears on account of the faster-growing $TiSi_2$ phase (see Fig. 5). The TiSi layer is too thin to be identified by x-ray diffraction, but the atomic concentration ratio derived from the backscattering spectrum corresponds to that of TiSi. No indication of such an initial TiSi layer was found in the spectra after annealing at a temperature of 500 °C or above. The same behavior has been observed in the Ti/Si(xtl) case as well, but at a temperature of about 500 °C.

Auger spectrometry was used for the depth profile measurement of impurities in the samples of Si(a)/Ti/Si(xtl). A small amount of carbon was found at the Ti–Si(stl) interface with a barely detectable amount of oxygen. However, the impurity levels at the Ti–Si(a) interface are below Auger detection limit.

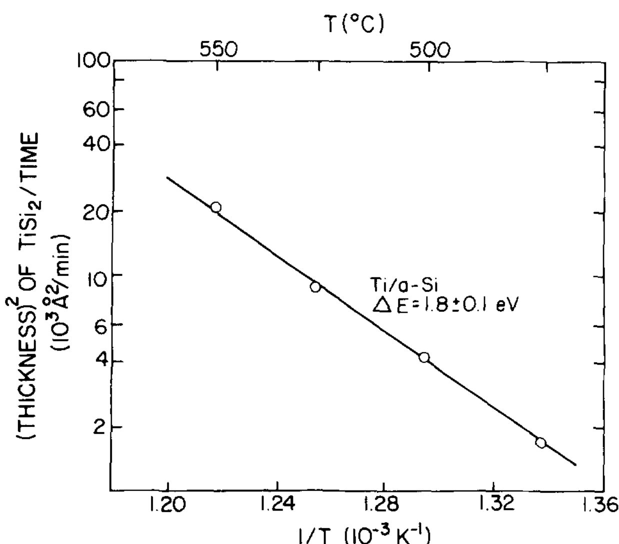

FIG. 4. Arrhenius plots for the growth rates of $TiSi_2$.

IV. DISCUSSION

Our results show the significance of the method of sample preparation in determining solid-phase reactions. We believe that the interface of the Ti–Si(a) is quite clean compared with that of the Ti–Si(xtl). It is known that the Si substrate prepared by a conventional chemical cleaning procedure contains oxide and other impurities. The amount of oxygen reaches $0.5–1\times10^{14}/cm^2$, even using HF solution as a final rinse before loading into the vacuum chamber.[10] Moreover, in the present study, Auger depth profile measurements show the presence of C at the Ti–Si(xtl) interface as well. The Ti–Si(a) interface is relatively contamination free, since the sample has been prepared with consecutive deposition of Si and Ti on the SiO_2 substrate without breaking the vacuum.

Besides the cleanliness of the Ti–Si(a) interface another factor that may be responsible for altering the reaction kinetics is the amorphous nature of the Si films. An amorphous Si layer deposited on a SiO_2 substrate was exposed to air for one day and then chemically cleaned following the identical procedure applied to the Si(xtl) substrate before the Ti layer was laid down. This sample thus consisted of Si(a) as the substrate, but had a surface prepared similarly to that of a Si(xtl) substrate. The reaction rate was then measured and found to be reduced to roughly that of Ti/Si(xtl) samples. This result suggests that the amorphous nature is not the primary factor for the difference in reaction kinetics.

It has been shown that by ion irradiation, the interfacial contaminants between a metal layer and substrate can be rendered ineffective, thus allowing silicide formation to proceed as if the oxide layer was absent.[11] We irradiated the Ti films (~400 Å thick) on ⟨100⟩ Si substrate, with 300-keV Xe^+ ions to a dose of 2×10^{14} Xe/cm^2 at 200 °C. Under this condition, the peak of Xe distribution is near the Ti–Si(xtl) interface and the maximum concentration of implanted Xe is less than 0.1 at %. The interfacial mixing produced at this low dose is barely detectable in the backscattering spectrum. The channeling measurement showed that the substrate was damaged, but not amorphous. Thermal annealing of those samples results in the formation of $TiSi_2$ with growth rates similar to those observed in Ti/Si(a) samples. The reduced reactivity of Ti films on Si(xlt) must therefore derive primarily from the impurities at the Ti–Si(xtl) interface. Support for this view is also found in the spectra of Fig. 1 where the Ti–Si(xtl) interface after a 39-min anneal at 525 °C is seen to be noticeably broader than the other interfaces, even though the reaction between x–Si and Ti has barely begun. Such a broad interface is typical for laterally nonuniform reactions, as one would expect to find if interfacial impurities dominate the reaction process. The nonreproducibility of the kinetics of reaction of early transition metal films with Si(xtl) substrates can now be explained partly in the same way.

The parabolic time dependence in the growth of Ti–

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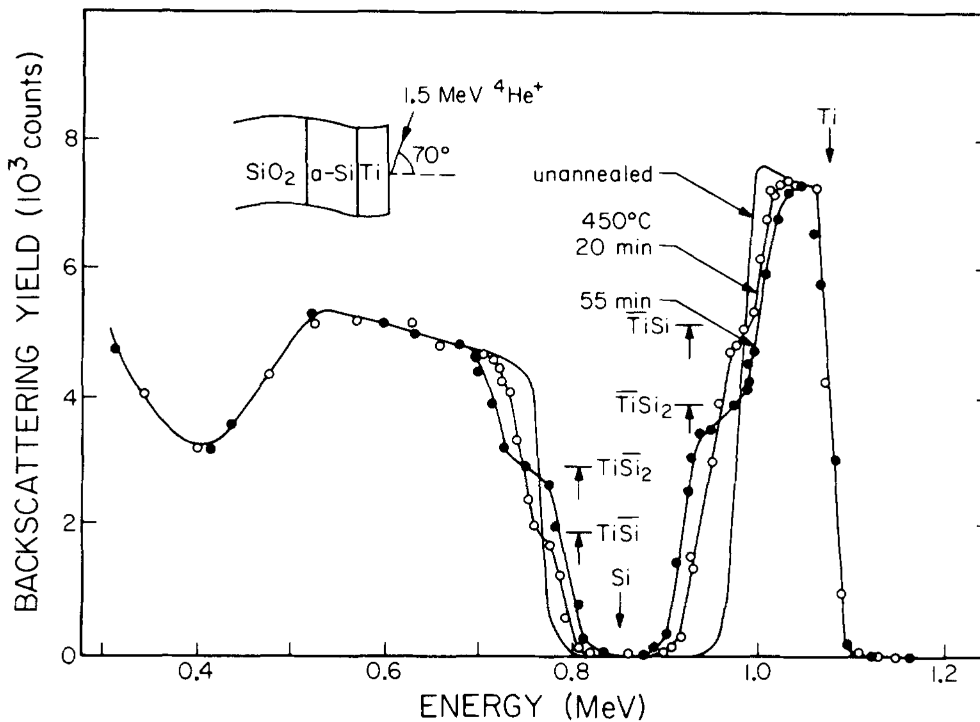

FIG. 5. 1.5-MeV $^4He^+$ backscattering spectra of Ti/Si(a) samples annealed at 450 °C showing that TiSi forms first and then is taken over by the formation of $TiSi_2$.

silicide is different from the linear time dependence usually observed for the formation of Si-rich refractory-metal silicides, such as $CrSi_2$, $MoSi_2$, and $TaSi_2$. Nevertheless, a recent study[12] revealed that the samples of Nb deposited on Si substrates at a pressure $> 2 \times 10^{-6}$ Torr show linear time dependence of $NbSi_2$ thickness, whereas the samples prepared under UHV conditions exhibit quadratic dependence. This quadratic dependence has also been observed in the growth of $MoSi_2$ (Ref. 12), when care is taken in the sample preparation.

There have been few measurements of the reaction kinetics in the Ti/Si system. Revesz *et al.*[13,14] have studied the lateral growth of Ti-silicide in the temperature range 750–900 °C and found that the growth is parabolic in time with the activation energy of 1.9 eV, which is quite consistant with our results. Bentini[15] studies the thermal reacton of Ti on Si for comparison with laser and electron beam irradiation. There was $\cong 30$ at. % oxygen in their Ti films and consequently formation temperature was shifted higher ($\cong 600$ °C) than in the present case ($\cong 450$ °C).

It has been observed in the present study that the TiSi phase forms first, and then is taken over by the formation of $TiSi_2$ for the Ti/Si(a) samples annealed at 450 °C. The similar results have also been reported for the sputtered Ti on Si annealed at 600 °C.[5] More recently, Bene and Yang[16] have studied the solid state nucleation in the Ti–Si ultrathin film system and concluded that the first compound formed is a metastable super structure identified as TiSi phase.

The accepted view is that early transition metal films react with a Si substrate by forming an interfacial layer of composition MSi_2. This compound is also that predicted by the Walser–Bene rule.[17] It seems that TiSi formed prior to $TiSi_2$ either goes against this rule and the accepted view, or results from the alteration of the phase formation sequence due to the presence of undetected impurities. It is known that annealing a metal–platinum compound deposited on Si, such as a Pt–Cr alloy on Si,[18] produces the formation of PtSi. The alteration of the phase formation sequence has also been found in Pt films on Si due to the presence of oxygen.[19] As the oxygen accumulates at the Pt_2Si–Si interface, the supply of the Pt to that interface is reduced and PtSi, the phase that normally appears when all the Pt is consumed, forms, and grows. Early results show that Si is the diffusing species in the formation of $TiSi_2$. Since Ti is extremely reactive, Ti oxides may form at Ti–Si interface and act as a "barrier" for the Si motion. Consequently, the supply of Si through that interface has been reduced and results in the formation of TiSi, next phase richer in Ti. After the impurities have been dispersed by the formation of TiSi, the supply of Si becomes sufficient so that the TiSi is soon taken over by the formation of $TiSi_2$. At a high temperature the Si becomes so mobile that the TiSi is taken over by the $TiSi_2$ phase in such a short time that the detection of TiSi is rather difficult. The temperature at which the formation of $TiSi_2$ sets in depends on the cleanliness at the Ti–Si interface which turns out to be 450 °C for Ti consecutively deposited on Si, 500 °C for Ti deposited on Si(xtl) using HF dip as a final rinse and 600 °C for sputtered Ti on Si.[5,16].

V. CONCLUSION

Our results show that Ti thin films on Si(a) layers deposited sequentially in a dry high vacuum form a $TiSi_2$ interfacial layer upon annealing at about 500 °C in vacuum. The growth of the $TiSi_2$ layer shows a transport-limited ($\propto \sqrt{\tau}$) behavior. The growth rate is reproducible and has an activation energy of 1.8 eV ($475 \leqslant T \leqslant 550$ °C). Titanium films deposited on amorphous or single-crystalline Si substrates that have been exposed to air and cleaned by standard chemical

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treatments prior to the Ti deposition do not exhibit a similarly reproducible growth rate, require higher temperatures for reaction and have rougher $TiSi_2$–Si interfaces than consecutively deposited Ti/Si(*a*) bilayers. We believe that it is the interfacial cleanliness that controls these reactions.

Above 500 °C, the Ti–Si(*a*) interface is clean enough to fully accommodate the influx of the diffusing Si and the Si-rich $TiSi_2$ phase forms by a transport-limited process. By contrast,the Ti–Si(*xtl*) interface contains impurities (e.g., O,C) that interfere with the diffusing Si and retard the formation of $TiSi_2$. Irradiation of that interface with energetic Xe ions disperses those impurities sufficiently to reestablish the transport-limited growth of $TiSi_2$ even though the Si substrate is not amorphized by the irradiation. Below 500 °C, TiSi formed initially on Ti/Si(*a*), presumably because residual impurities suppress the Si flux and the resulting kinetics favors the growth of TiSi.

ACKNOWLEDGMENTS

We acknowledge B. Y. Tsaur for the initiation of the present experiments, R. Fernandez and R. Gorris for the technial assistance, and L. Rathbun for Auger measurements. The work was supported in part by the Office of Naval Research (L. R. Cooper) and by NSF through the National Research and Resource Facility for Submicron Structures.

[1]G. Ottaviani and J. W. Mayer in *Reliability and Degradation*, edited by M. J. Howes and D. V. Morgan (Wiley, New York, 1981), Chap. 2.
[2]B. W. Bower and J. W. Mayer, Appl. Phys. Lett. **20**, 359 (1972).
[3]W. K. Chu, S. S. Lau, J. W. Mayer, H. Muller, and K. N. Tu, Thin Solid Films **25**, 393 (1975).
[4]H. Kato and Y. Nakamura, Thin Solid Films **34**, 135 (1976).
[5]S. P. Murarka and D. B. Fraser, J. Appl. Phys. **51**, 342 (1980).
[6]H. Krautle, M-A. Nicolet, and J. W. Mayer, J. Appl. Phys. **45**, 3304 (1974).
[7]B. I. Formin, A. E. Gershinskii, E. I. Cherepou, and F. L. Edelman, Phys. Status Solidi A **36**, K89 (1976).
[8]R. J. Wagner, S. S. Lau, J. W. Mayer, and J. A. Roth, in *Proceedings of the Symposium on Thin Film Phenomena-Interfaces and Interactions*, edited by J. E. E. Baglin and J. M. Poate (Electrochemical Society, New York, 1978), Vol. 78-2, p. 59.
[9]A. Guivarch, P. Auvray, L. Berthou, M. Lecun, J. P. Boulet, P. Henoc, G. Pelous, and A. Martinez, J. Appl. Phys. **49**, 233 (1978).
[10]L. S. Hung, S. S. Lau, M. Von Allmen, J. W. Mayer, B. M. Ullrich, J. E. Baker, P. Williams, and W. F. Tseng, Appl. Phys. Lett. **37**, 909 (1980).
[11]L. S. Wielunski, C. D. Lien, B. X. Liu, and M-A. Nicolet, J. Vac. Sci. Technol. **20**, 175 (1982).
[12]P. Cappelletti, F. Mori, G. Pignatel, G. Ferla, F. Nava, and G. Ottaviani (private communication).
[13]P. Revesz, J. Gyimesi, L. Pogany, and G. Peto, Proceeding of the MRS, Boston, 1982 (to be published).
[14]P. Revesz, J. Gyimesi, L. Pogany, and G. Peto, J. Appl. Phys. **54**, 2114 (1983).
[15]G. G. Bentini, M. Servidori, C. Cohen, R. Nipoti, and A. V. Drigo, J. Appl. Phys. **53**, 1525 (1982).
[16]R. W. Bene and H. Y. Yang, J. Electron. Mater. **12**, 1 (1983).
[17]R. M. Walser and R. W. Bene, Appl. Phys. Lett. **28**, 624 (1976).
[18]K. N. Tu, W. N. Hammer, and J. O. Olowolafe, J. Appl. Phys. **51**, 1663 (1980).
[19]C. Canali, C. Catellani, M. Prudenziati, W. H. Wadlin, and C. A. Evans, Appl. Phys. Lett. **31**, 43 (1977).

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