PHYSICAL REVIEW B VOLUME 22, NUMBER 4 15 AUGUST 1980

^{31}Si tracer studies of the oxidation of Si, CoSi$_2$, and PtSi

R. Pretorius, W. Strydom, and J. W. Mayer*
Southern Universities Nuclear Institute, P.O. Box 17, Faure 7131, South Africa

C. Comrie
Physics Department, University of Cape Town, Rondebosch 7700, South Africa
(Received 24 March 1980)

Radioactive ^{31}Si ($T_{1/2}=2.62$ hours) was used to study the mechanism of atmospheric steam oxidation of silicon, CoSi$_2$, and PtSi. Measurement of the radioactivity profile in the SiO$_2$ layer formed on Si shows that oxide growth takes place at the Si-SiO$_2$ interface by oxygen diffusion through the growing SiO$_2$ layer. The sharpness of the measured activity profile also indicates that Si is very immobile in SiO$_2$ at the oxidation temperature of 1000 °C. The oxidation studies on CoSi$_2$ and PtSi also show that SiO$_2$ formation takes place at the silicide-SiO$_2$ interface and that oxygen is the diffusing species through the SiO$_2$ layer. By marking these silicides with ^{31}Si and measuring the radioactivity left in the silicide layer as a function of SiO$_2$ thickness, it was shown that silicon diffuses through the silicide by a substitutional (vacancy) diffusion mechanism. Nonradioactive silicon supplied from the underlying silicon substrate mixes completely with the radioactive silicon in the silicide layer, owing to the high silicon self-diffusion coefficients in both CoSi$_2$ and PtSi at the oxidation temperatures used.

I. INTRODUCTION

In silicon semiconductor technology the formation of an insulating layer of SiO$_2$ is crucial for photolithography, isolation of devices and interconnections, and final passivation of devices. The thermal growth of such SiO$_2$ films on silicon has been extensively studied using various oxidants, namely, dry oxygen,[1-9] wet oxygen,[3,4,6,7,9] and steam[2,3,5,7] at temperatures ranging from about 700 to 1300 °C. For all these oxidizing conditions it is generally found that following the initial growth, the thickness of the formed SiO$_2$ layer is proportional to the square root of time, thereby indicating that the oxidation process is diffusion limited. For SiO$_2$ thicknesses less than about 350 Å the growth is found to be approximately linear with time.[4,9]

Oxidation in steam or wet oxygen proceeds much faster than in dry oxygen[3,5,7,9] and is thought to be due to the fact that the H$_2$O acts both as an additional source of oxidant and as an accelerator for the oxidation process. It is postulated that this latter effect occurs because the H$_2$O modifies the SiO$_2$ network, thereby enhancing diffusion of the primary oxidant through the SiO$_2$ film.[9]

There has also been much interest in the oxidation of the metal silicides.[10-12] These silicides are extensively used as ohmic or rectifying contacts to silicon devices and advantage has been taken of the good electrical conductivity of some of the metal silicides for the fabrication of gates for field-effect transistors.[13,14] For such applications it is necessary to cover the metal silicide with an insulating layer, such as SiO$_2$, so as to enable the use of overcrossing conductors in subsequent layers.

The most commonly considered mechanism for oxide growth on silicon is that of oxygen diffusion through the growing SiO$_2$ layer and reaction with elemental silicon at the advancing Si-SiO$_2$ interface. Such a mechanism can be related to the presence of micropores and microchannels in the SiO$_2$ films.[15,16] This model seems to be confirmed by ^{18}O tracer studies carried out during high-pressure steam[2] and dry oxygen[17] oxidation of silicon. No work has, however, yet been carried out on the mechanism of metal-silicide oxidation. In this investigation we have used radioactive ^{31}Si as a tracer to study the thermal oxidation of Si, CoSi$_2$, and PtSi in steam at atmospheric pressure.

II. EXPERIMENTAL

^{31}Si was produced by irradiating high-purity silicon chips of irregular shapes and sizes in a nuclear reactor with a neutron flux of 2.5×10^{13} neutrons per cm^2 per sec. During neutron activation ^{31}Si is formed from ^{30}Si (3.1 at. %) by the reaction $^{30}\mathrm{Si}(n,\gamma)^{31}\mathrm{Si}$ which has a cross section of 0.10 b. ^{31}Si decays with a half-life of 2.62 hours by emitting beta particles (max β^- energy is 1.48 MeV) for 99.93% of its disintegrations. The ^{31}Si activity was measured with an end-window Geiger counter.

Silicon substrates, 10 Ω cm and (100) orientation, were cleaned by conventional methods before loading into the *e*-gun evaporation chamber. Before evaporation of the radioactive silicon, care was taken first to clean it in organic solvents and distilled water, followed by a HF:HNO_3 etch, in order to remove any possible interfering radioactivity due to surface contamination which could have taken place prior to irradiation in the nuclear reactor. Between 300 and 400 Å of radioactive silicon was usually deposited. For the oxidation studies of $CoSi_2$ and PtSi approximately 350 Å of Co and 500 Å of Pt were deposited on top of the radioactive silicon layer. These thicknesses were more than sufficient to consume all the radioactive ^{31}Si during silicide formation. All depositions were carried out at a pressure of $\sim 10^{-7}$ Torr and thicknesses were monitored with a quartz Inficon Thickness Monitor.

The Co and Pt samples were first annealed at 800 °C for 10 minutes in a vacuum tube furnace at pressures below 1×10^{-6} Torr, in order to form $CoSi_2$ and PtSi. Oxidation of the silicon, $CoSi_2$, and PtSi samples was carried out at 1000 °C in a tube furnace through which steam flowed at atmospheric pressures. The position or activity profile of the radioactive ^{31}Si in the sample was determined by a combination of rf sputter etching, radioactivity measurement, and Rutherford backscattering.

III. RESULTS AND DISCUSSION

A. Oxidation of silicon

When the Si (100) samples with 300 to 400 Å of radioactive silicon are oxidized at 1000 °C, a band of radioactive SiO_2 is first formed with the radioactive silicon. Upon further oxidation (see Fig. 1) this band of radioactive SiO_2 can move to the surface of the sample if SiO_2 formation takes place by substitutional (vacancy) diffusion of silicon through the SiO_2 layer or by oxygen diffusion through the SiO_2 layer, with SiO_2 formation taking place at the Si-SiO_2 interface. However, if the band of radioactive SiO_2 stays at the Si-SiO_2 interface, it can be deduced that Si diffuses by interstitial or grain-boundary diffusion to the surface of the SiO_2 layer to react with the oxidizing species to form SiO_2. Grain-boundary diffusion can, however, not take place in SiO_2 because of the absence of grains. Apart from the two limiting cases mentioned above the radioactive ^{31}Si marker could be located somewhere in the middle of the SiO_2 layer if SiO_2 formation takes place by diffusion of both the silicon and oxygen, the exact position depending on the relative diffusion rates of both species.

The activity profile in the SiO_2 layer after oxidation of silicon is given in Fig. 2. The calculated activity profile at the SiO_2 silicon substrate interface immediately after initial radioactive SiO_2 formation is shown by the dashed lines. The presence of the activity at the surface of the formed SiO_2 layer indicates that the oxygen is the diffusion species through the SiO_2 and that SiO_2 formation takes place at the Si-SiO_2 interface, or that silicon diffuses by a substitutional (vacancy) diffusion mechanism through the SiO_2 layer, thereby "pushing" or displacing the radioactive Si atoms to the surface of the formed SiO_2, where they react with oxygen to form a layer of radioactive SiO_2. However, when the sample shown in Fig. 2 is heated up to temperatures as high as 1200 °C, the band of radioactive SiO_2 still remains as a sharp profile at the surface of the sample thereby indicating that the silicon atoms are very immobile in the formed SiO_2 layer. We therefore conclude that SiO_2 formation takes place by oxygen diffusion or by the diffusion of some oxygen species through the SiO_2 layer with further SiO_2 formation taking place at the Si-SiO_2 interface. These results are in agreement with previous ^{18}O tracer experiments.[2,17]

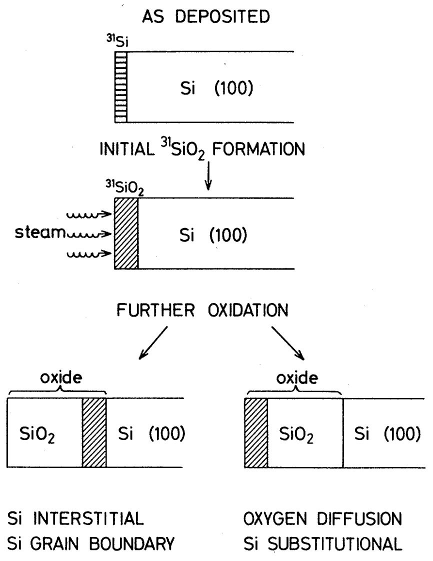

FIG. 1. Schematic diagram showing how radioactive ^{31}Si can be used to determine the diffusing species and diffusion mechanism during the oxidation of silicon. If the band of radioactive $^{31}SiO_2$ is located at the Si-SiO_2 interface it can be deduced that silicon diffuses by an interstitial or grain-boundary mechanism. If oxygen is the diffusing species through the growing SiO_2 layer, or if silicon diffuses by a substitutional (vacancy) mechanism, the band of activity will be on the sample surface. If both Si and oxygen diffuse, the band of radioactive ^{31}Si marker could be located somewhere in the middle of the SiO_2.

B. Oxidation of $CoSi_2$ and PtSi

Rutherford backscattering spectra of the as-deposited virgin sample, after $CoSi_2$ formation at 800 °C for 10 minutes after steam oxidation at

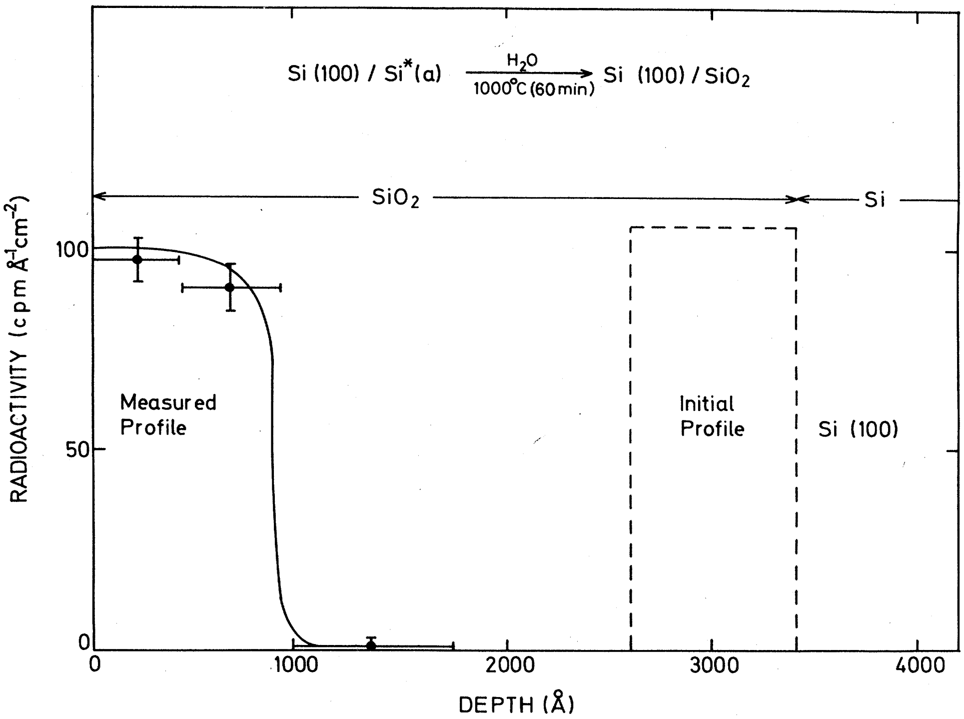

FIG. 2. ^{31}Si activity profile measured in SiO$_2$, which was formed by oxidizing silicon in steam for 60 minutes at 1000 °C. The calculated activity profile after initial ^{31}SiO$_2$ formation is also shown (see dashed lines).

1000 °C for 30 minutes, are shown in Fig. 3. The thickness of the formed SiO$_2$ layer was determined by measurement of the width of the oxygen signal, the width of the step due to silicon in the SiO$_2$ layer, and by determining the shift of the front edge of the Co signal with respect to its surface position. These three values were internally consistent and an average value was used. These measurements show that the thickness of the formed SiO$_2$ layer is also proportional to the square root of time, as is the case for silicon (Fig. 4), thereby indicating a diffusion limited process. It is interesting to note that the oxidation rate for CoSi$_2$ is much larger than that for silicon.

The fraction of the activity left in the CoSi$_2$ layer after SiO$_2$ formation was determined by removing the SiO$_2$ layer by rf ion-beam sputtering and measuring the activity in the sample before and after removal of the SiO$_2$ layer. The removal of the SiO$_2$ layer was monitored by Rutherford backscattering.

In Fig. 5 the percentage of radioactive ^{31}Si left in the CoSi$_2$ layer after thermal oxidation in steam at 1000 °C is given as a function of the normalized thickness (D value) of the formed SiO$_2$ layer. By expressing the SiO$_2$ thickness as D, where D is the ratio between the number of Si atoms in SiO$_2$ and the number of Si atoms in the CoSi$_2$, a universal relationship is obtained which is independent of the thickness or type of metal silicide studied. Curves A, B, C, and D in Fig. 5 have been theoretically calculated for different mechanisms of silicon diffusion through the CoSi$_2$ layer.

Curve A. Substitutional (vacancy) diffusion. If silicon diffuses through the CoSi$_2$ layer by a substitutional (vacancy) diffusion mechanism, the radioactive silicon atoms in the CoSi$_2$ layer will be effectively displaced toward the surface by nonradioactive silicon atoms entering from the single-crystal silicon substrate. As would be expected in this model, all the radioactive silicon atoms will be displaced from the CoSi$_2$ layer for $D = 1$ and the percentage activity left in the CoSi$_2$ will be zero. In practice, however, this would only happen for D values slightly higher than one due to the statistical nature of diffusion. Silicon atoms supplied from the silicon substrate thus, in effect, "push" the radioactive silicon from the CoSi$_2$ layer into the growing SiO$_2$ film. This would be similar to the mechanism found for silicon diffusion through Pd$_2$Si during solid-phase epitaxial growth of silicon in the Si (100)-Pd$_2$Si-Si (amorphous) system.[18,19]

Curve B. Substitutional (vacancy) diffusion with high self-diffusion of silicon in the CoSi$_2$, and low self-diffusion of silicon in the SiO$_2$. At tempera-

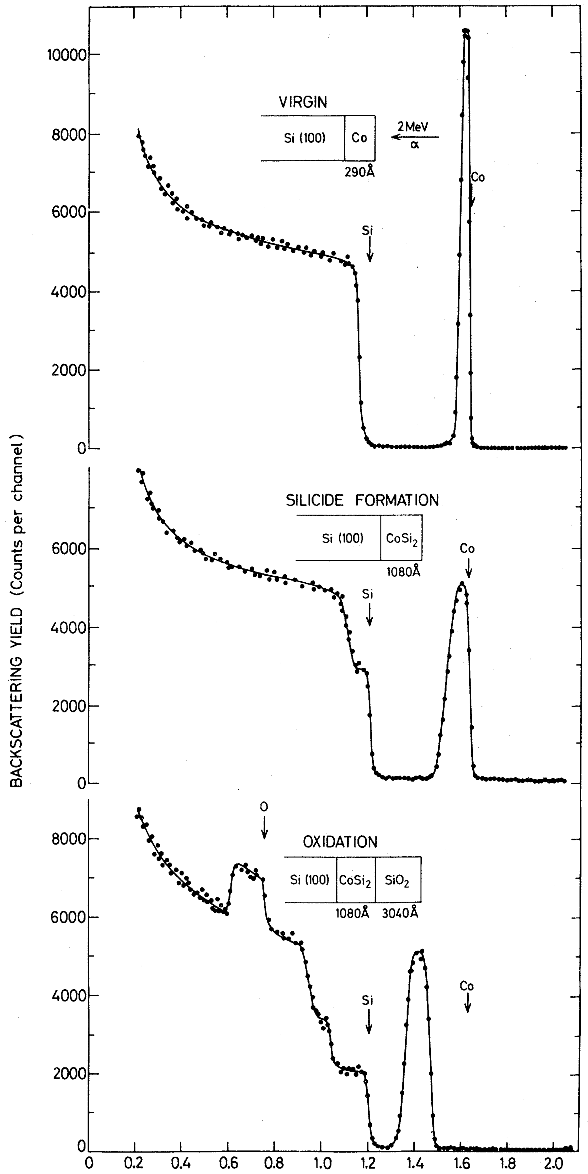

FIG. 3. Rutherford backscattering spectra showing $CoSi_2$ formation at 800 °C and the formation of a SiO_2 layer during atmospheric steam oxidation at 1000 °C for 30 minutes. The arrows indicate the energies of alpha particles scattered from the indicated elements, when located at the surface of the sample.

tures of about 570°C and higher, the self-diffusion rate of silicon in Pd_2Si and PtSi is so high that complete intermixing of radioactive and nonradioactive silicon atoms takes place in the silicide within 20 minutes.[20] If this were also true for $CoSi_2$ at the temperature of oxidation it is clear that all the radioactivity in the $CoSi_2$ layer can never be completely removed, regardless of how thick the grown SiO_2 layer is. Curve B in Fig. 5

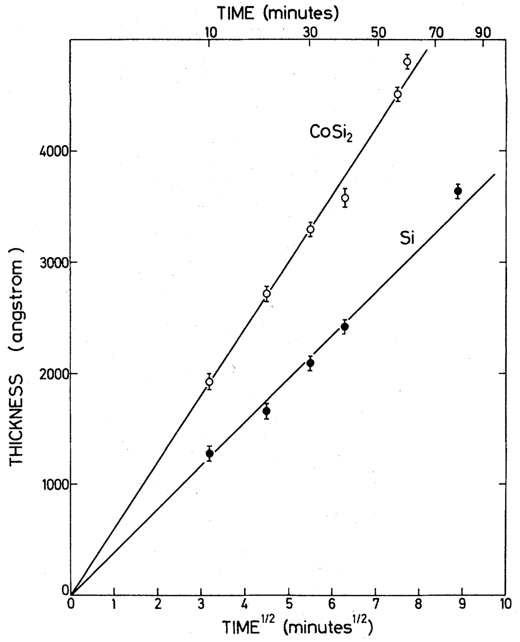

FIG. 4. Thickness of SiO_2 formed on a silicon and $CoSi_2$ sample as a function of steam oxidation time at 1000 °C. The silicon sample consisted of a Si (100) substrate onto which 400 Å amorphous silicon was deposited. The square root dependence on time indicates a diffusion limited process.

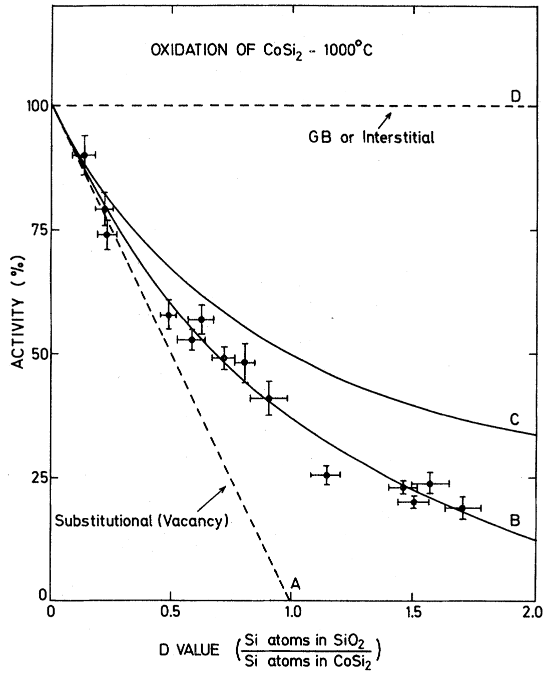

FIG. 5. Percentage ^{31}Si activity left in the $CoSi_2$ layer after oxidation at 1000 °C as a function of SiO_2 thickness (D value). A, B, C, and D are theoretical curves calculated for different silicon diffusion mechanisms through the $CoSi_2$ layer (see text).

was calculated for conditions such that complete equilibrium is immediately obtained between radioactive silicon atoms in the $CoSi_2$ layer and nonradioactive silicon atoms entering from the silicon substrate. As the SiO_2 layer grows, the percentage activity in the $CoSi_2$ layer will decrease exponentially with D, and curve B is thus given by

$$A = 100\, e^{-D} \,, \qquad (1)$$

where A is the percent activity.

Curve C. Substitutional (vacancy) diffusion with high silicon self-diffusion in both the $CoSi_2$ and SiO_2 layer. In this case complete intermixing between radioactive and nonradioactive silicon atoms takes place throughout both the $CoSi_2$ and SiO_2 layer. The relationship between the percentage activity left in the $CoSi_2$ layer and D is then given by

$$A = 100/(1 + D) \,. \qquad (2)$$

Curve D. Interstitial and/or grain boundary diffusion of Si through the $CoSi_2$ layer. Silicon could be supplied to the growing SiO_2 layer by grain-boundary and/or "pure" interstitial (no interaction with Si atoms in the $CoSi_2$ lattice) diffusion of non-radioactive silicon atoms directly from the single-crystal substrate. In this case no radioactive silicon atoms will be incorporated into the growing SiO_2 layer and the percentage activity in the $CoSi_2$ layer remains constant at 100%.

It is clear from Fig. 5 that our results for $CoSi_2$ oxidation at 1000 °C fit case B very well, which is in contrast to the study of $CrSi_2$ growth on Pd_2Si and PtSi, where curve C is approached at higher temperatures.[21] The results for the PtSi oxidation are given in Fig. 6, and again it is clear that measurements approach curve B, although not as closely as for $CoSi_2$ oxidation. The PtSi results were obtained at an oxidation temperature of 800 °C. At higher temperatures the PtSi layer tended to "ball up" badly.

For the case of $CoSi_2$ oxidation, radioactivity profiles in the grown SiO_2 layer were also determined. This activity profile is given in Fig. 7 and represents the results obtained from the oxidation of three separate samples. Care was taken to keep the thickness of the $CoSi_2$ layer in each sample the same. Rutherford backscattering showed that the samples had an average $CoSi_2$ thickness of 1230 ± 50 Å.

The activity profile in the SiO_2 layers grown on $CoSi_2$ (Fig. 7) shows that the highest concentration of radioactive ^{31}Si is at the surface of the sample and that the activity decreases exponentially as one moves to the $CoSi_2$-SiO_2 interface. The solid-line activity profile is calculated for conditions where silicon self-diffusion is very high in the $CoSi_2$ layer and very low in the SiO_2 layer and that oxygen or some other chemical form of oxygen is the diffusing species during SiO_2 growth. The first two conditions have already been proved to be the case as our results in Fig. 5 indicate. Proof of the very low self-diffusion of silicon in SiO_2 at 1000 °C is also given by the sharp activity profile obtained during silicon oxidation (see Fig. 2). Once the radioactive silicon originating from the $CoSi_2$ layer is thus bound to form SiO_2 it becomes immobile and its activity concentration in the SiO_2 gives a record of the radioactivity concentration in the $CoSi_2$ layer at that specific moment. For a silicon specific activity of 220 cpm/Å/cm^2 and a $CoSi_2$ thickness of 1230 Å the theoretical activity profile as a function of x, the depth of Angstroms in the SiO_2 layer, is given by

$$A = 33.2 \exp(-0.4636x/1230)$$

in cpm/Å/cm^2. The measured activity profile in Fig. 7 follows the theoretical activity profile reasonably well and thus provides direct proof that oxygen or some form of oxygen is the diffusing species through the growing SiO_2 layer and that growth takes place at the $CoSi_2$-SiO_2 interface. If silicon were the species diffusing through the SiO_2 layer, growth would have taken place on the surface of the sample and the highest ^{31}Si concentration would then have been at the $CoSi_2$-SiO_2 inter-

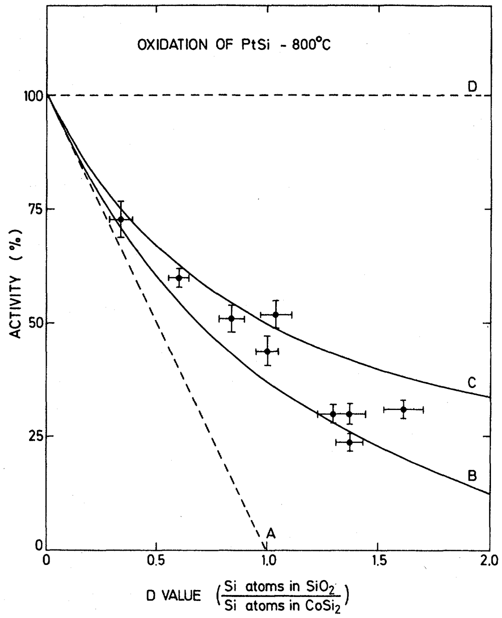

FIG. 6. Percentage ^{31}Si activity left in the PtSi layer after SiO_2 formation during oxidation in steam at 800 °C. The SiO_2 thickness formed is expressed as a D value, which is the ratio between the number of silicon atoms in the SiO_2 and in the $CoSi_2$.

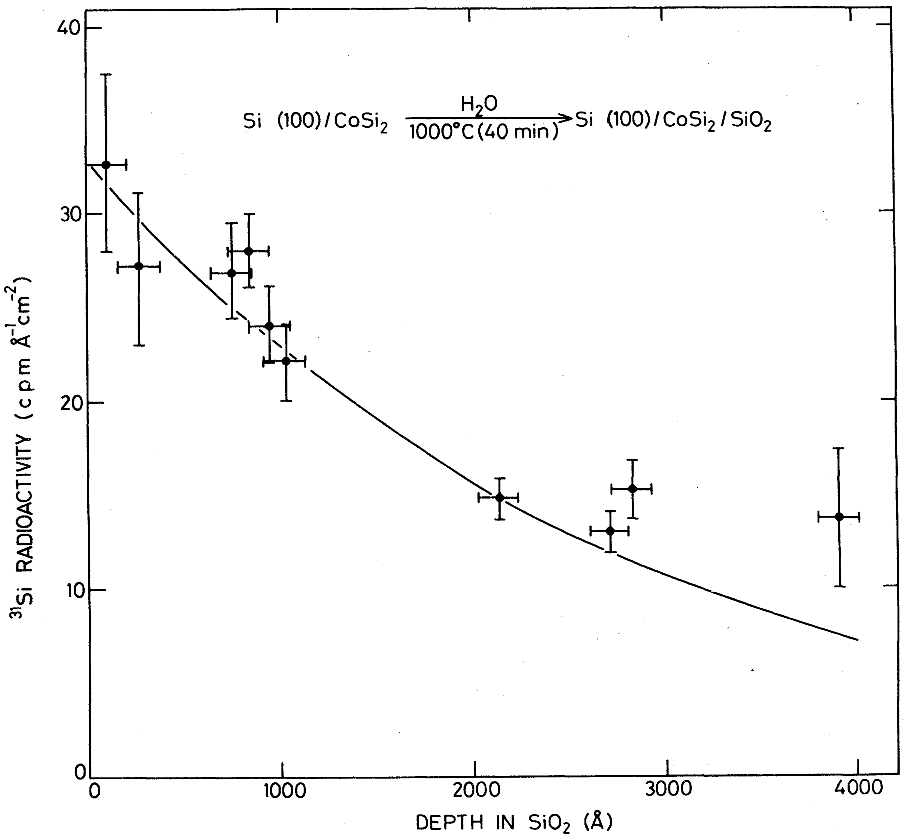

FIG. 7. Radioactivity profile measured in SiO_2 which was formed on $CoSi_2$ during steam oxidation at 1000 °C. The solid curve is calculated for conditions where silicon self-diffusion is very high in the $CoSi_2$ layer and very low in the SiO_2 layer and with the assumption that oxygen is the diffusing species through the SiO_2.

face, decreasing exponentially toward the sample surface.

IV. CONCLUSION

In the present work radiotracer measurements with ^{31}Si were made to investigate steam oxidation of silicon and $CoSi_2$ at 1000 °C and PtSi at 800 °C. The growth of SiO_2 on silicon is characterized by sharp radiotracer depth profiles in the SiO_2, which indicate that silicon has a very low mobility in SiO_2 at the oxidation temperature of 1000 °C. The surface location of the radioactive ^{31}Si indicates that oxide growth occurs by diffusion of oxygen to the Si-SiO_2 interface, in agreement with previous ^{18}O tracer measurements.

For $CoSi_2$ and PtSi oxidation, the residual radioactivity left in the silicide layer after SiO_2 formation shows that silicon diffuses through the silicide by a substitutional (vacancy) mechanism. Nonradioactive silicon supplied from the underlying silicon substrate mixes completely with the radioactive silicon in the silicide layer due to high silicon self-diffusion in the silicide itself. This mixing thus dilutes the amount of radioactive silicon available at the silicide-SiO_2 interface for subsequent incorporation in the growing SiO_2 layer. The activity depth profile measured within the SiO_2 layer formed on the $CoSi_2$ indicates that the growth of SiO_2 occurs at the $CoSi_2$-SiO_2 interface by oxygen diffusion through the growing SiO_2 layer. In this investigation it was not possible to obtain self-diffusion coefficients because of the high diffusivity at the temperatures used. Measurements are currently underway to determine self-diffusion coefficients of Si in various metal silicides at temperatures below those used in the current investigation. The present results show that the combination of Rutherford backscattering and ^{31}Si radiotracer studies can provide much basic information about thin-film interaction and interdiffusion in the solid state.

ACKNOWLEDGMENTS

This work was financially supported by the South African Council for Scientific and Industrial Research and the South African Atomic Energy Board.

*Present address: California Institute of Technology, Pasadena, California.

[1] J. T. Law, J. Phys. Chem. 61, 1200 (1957).

[2] J. R. Ligenza and W. G. Spitzer, J. Phys. Chem. Solids 14, 131 (1960).

[3] B. E. Deal, J. Electrochem. Soc. 110, 527 (1963).

[4] B. E. Deal and A. S. Grove, J. Appl. Phys. 36, 3770 (1965).

[5] H. C. Evitts, H. W. Cooper, and S. S. Flaschen, J. Electrochem. Soc. 111, 688 (1964).

[6] B. E. Deal and M. Sklar, J. Electrochem. Soc. 112, 430 (1965).

[7] F. W. Ainger, J. Mater. Sci. 1, 1 (1966).

[8] E. A. Irene and Y. J. van der Meulen, J. Electrochem. Soc. 123, 1380 (1976).

[9] E. A. Irene and R. Ghez, J. Electrochem. Soc. 124, 1757 (1977).

[10] S. Zirinsky, W. Hammer, F. d'Heurle, and J. Baglin, Appl. Phys. Lett. 33, 76 (1978).

[11] F. Mohammadi, K. C. Saraswat, and J. D. Meindl, Appl. Phys. Lett. 35, 529 (1979).

[12] J. B. Berkowitz-Mattuck and R. K. Dils, J. Electrochem. Soc. 112, 583 (1965).

[13] T. Mochizuki, K. Shibata, T. Inoue, K. Ohuci, and M. Kashigawi, Extended Abstracts, Electrochemical Society Meeting (1977), Vol. 77-2, p. 331 (unpublished).

[14] B. L. Crowder, S. Zirinsky, and L. Ephrath, Recent News, No. 464, Electrochemical Society Meeting (1977) (unpublished).

[15] S. W. Ing, R. E. Morrison, and J. E. Sandor, J. Electrochem. Soc. 109, 221 (1962).

[16] E. A. Irene, J. Electrochem. Soc. 125, 1708 (1978).

[17] E. Rosencher, A. Straboni, S. Rigo, and G. Amsel, Appl. Phys. Lett. 34, 254 (1979).

[18] R. Pretorius, Z. L. Liau, S. S. Lau, and M.-A. Nicolet, Appl. Phys. Lett. 29, 598 (1976).

[19] R. Pretorius, Z. L. Liau, S. S. Lau, and M.-A. Nicolet, J. Appl. Phys. 48, 2886 (1977).

[20] R. Pretorius, J. Electrochem. Soc. (in press).

[21] R. Pretorius, J. O. Olowolafe, and J. W. Mayer, Philos. Mag. 37, 327 (1978).