

Effects of a thin SiO₂ layer on the formation of metal–silicon contacts

Cite as: Journal of Vacuum Science and Technology **18**, 949 (1981); <https://doi.org/10.1116/1.570962>
Published Online: 04 June 1998

S. M. Goodnick, M. Fathipour, D. L. Ellsworth, and C. W. Wilmsen



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[Growth of native oxide on a silicon surface](#)

Journal of Applied Physics **68**, 1272 (1990); <https://doi.org/10.1063/1.347181>

[Defect formation in SiO₂/Si\(100\) by metal diffusion and reaction](#)

Applied Physics Letters **53**, 589 (1988); <https://doi.org/10.1063/1.100630>

[Effectiveness of SiO₂ for preventing silicon -metal reactions at high temperatures](#)

Journal of Applied Physics **51**, 5390 (1980); <https://doi.org/10.1063/1.327456>



Effects of a thin SiO₂ layer on the formation of metal-silicon contacts

S. M. Goodnick, M. Fathipour, D. L. Ellsworth, and C. W. Wilmsen

Colorado State University, Fort Collins, Colorado 80523

(Received 18 September 1980; accepted 2 January 1981)

The reactions that occur between different metals and silicon wafers with a thin oxide layer have been investigated. The oxides were formed by either exposing the chemically cleaned wafer to air at room temperature or by thermally growing 30 Å of oxide at 700 °C in dry O₂. Al, Pt, and Au contacts were investigated. The interfacial reactions before and after heat treatment at 400 °C for 1 h were characterized using Auger and ESCA sputter profiling. The air grown oxides were found not to prevent intimate contact between the metal and the silicon, and reactions were observed for both heat treated and unheated samples. At 400 °C the 30 Å thermal oxide was found to be an effective diffusion barrier for Pt but less effective for Au. The Al reduced the 30 Å of SiO₂ to form Al₂O₃ at the interface in what appeared to be a self-limiting reaction. A comparison between the reactions observed on air grown oxides and 30 Å of thermally grown oxide are consistent with observations that the room temperature oxides are not as fully formed as oxides grown at 700 °C.

PACS numbers: 82.80.Pv, 82.65.JV, 85.30.Hi, 81.40. — z

I. INTRODUCTION

The continued shrinkage of device dimensions in VLSI technology has increasingly focused attention on the need for detailed understanding of contact metallization processes. The complex chemical and electronic interaction of various deposited metals with silicon substrates has been the subject of numerous investigations.¹⁻⁴ The Schottky barrier that forms upon intimate contact between metals and covalent semiconductors such as silicon is found to be only weakly dependent on the metal chosen. This exemplifies the so-called "Bardeen limit"⁵ of barrier formation in which the semiconductor Fermi level is pinned at the surface due to interface states.

Characterization of the intimate metal silicon contact using a host of analytical surface techniques has revealed that the metal-silicon interface is chemically quite active and that its electronic nature is in many ways inadequately described by the Bardeen model.^{6,7} Many metals react at low temperature with silicon to form one or more stable bulk compounds (silicides). Other metals, while not chemically reactive, readily dissolve elemental Si at the interface giving rise to widespread interdiffusion in the contact region.⁸ Thus, any representation of the metal-silicon contact as an abrupt junction is approximate at best.

The presence of a thin interfacial oxide at metal-silicon interfaces may have a profound effect on the formation of Schottky barriers. If the oxide is too thick, current flow in the resulting device may be severely suppressed, accompanied by a loss of rectifying characteristics. However, an oxide layer that is sufficiently thin may sustain considerable current via tunneling.⁹ A thin interfacial oxide also may significantly reduce the density of interface states by satisfying silicon dangling bonds. As a result, the Fermi level at the surface may become unpinned and the barrier height is more directly determined by the metal work function. In addition, a thin interfacial layer may act as a barrier to the chemical reaction

and interdiffusion that characterizes the intimate metal silicon contact. Thus, the presence of a thin oxide at the interface acts as a passivating influence, both from an electronic and a chemical standpoint.

The focus of the present investigation has been to observe the influence of thin SiO₂ layers on the chemical formation of metal-silicon contacts. Three metals were investigated (Al, Pt, and Au) each unique in its expected reaction with the Si-SiO₂ substrate. Al does not form any bulk compounds with Si, rather it forms a eutectic. However, Al₂O₃ has a higher heat of formation (399 kcal/mole) than that of SiO₂ (203 kcal/mole), and thus is expected, from thermodynamic considerations, to reduce the thin SiO₂ layer. Pt readily forms a stable silicide, however it does not form a strong oxide and thus is not expected to reduce the SiO₂ layer. Au represents an "inert" material as it neither forms a stable silicide nor a thermodynamically more stable oxide than SiO₂. Nevertheless, several metastable phases have been shown to exist at the Au-Si interface,¹⁰⁻¹² and at high temperature, the Au has been found to diffuse through thick SiO₂ layers and cause dissolution of the oxide.^{13,14} Thus the Au-SiO₂-Si system is probably the most complicated of the three systems reported here.

II. EXPERIMENT

The silicon substrates used in this study were commercial single crystal (100) wafers, phosphorous doped to 10¹⁵ cm⁻³. The wafers were chemically cleaned using standard organic solvents followed by etching in a 4:1 solution of HF and ammonium fluoride. This was accompanied by rinsing in successive peroxide solutions of NH₄OH and HCl. This latter step is effective in removing metallic ions from the silicon surface. Finally, the wafers were rinsed in ultrapure deionized water prior to oxidation.

Thin SiO₂ layers were grown in dry oxygen at 700 °C in an open tube furnace. The oxides were grown to approximately 30 Å as determined ellipsometrically. Half of each wafer was

etched again in HF and both halves were immediately placed in the vacuum system for metallization. A Si wafer thermally oxidized to 1000 Å was also included.

Thin metal layers less than 200 Å thick were thermally evaporated at a background pressure of approximately 7×10^{-7} Torr (9.3×10^{-5} Pa). Both Pt and Al were evaporated from tungsten filaments while Au was deposited from a molybdenum boat. The film thickness was controlled using a Sloan quartz oscillator rate deposition monitor.

Post deposition heating was performed under vacuum with samples heated to 400°C for 1 h and allowed to slowly cool. The resulting structures were transferred to a combined AES/XPS system described previously.¹⁵ In addition, scanning electron micrographs coupled with x-ray dispersive techniques were used to observe any topological phenomena such as agglomeration that might have occurred.

AES and XPS data were digitally acquired and processed, with XPS peak intensity and location obtained through non-linear least squares fitting procedures. To eliminate overlap effects of separate Auger signals, a linear least square mixing of standardized pure material spectra was employed to determine the relative amounts of various materials present. The method was successful in cases where pure standards were available but failed in cases where non-bulk phases existed, such as occurs at the intimate Au-Si interface.

III. DISCUSSION AND RESULTS

A. Pt-SiO₂-Si

Current literature reflects a fairly clear understanding of the mechanisms and kinetics of platinum silicide growth. At temperatures above 200°C, the silicide growth is initiated by the formation of a metal rich Pt₂Si phase at the Pt-Si interface. Marker experiments¹⁶ seem to indicate that during the formation of the Pt₂Si layer both Si and Pt are diffusing through the silicide, although at lower temperatures Pt appears to be the faster species. The formation of di-platinum silicide is followed by the appearance of the thermodynamically favored PtSi once the supply of free platinum is hindered or exhausted. PtSi forms at the Pt₂Si-PtSi interface primarily by diffusion of Si through the PtSi phase.¹⁷

It has been shown by Canali¹⁸ and Crider,¹⁹ that the rate and extent of Pt₂Si formation is critically dependent on the presence of impurities, especially oxygen, incorporated in the Pt film. In the absence of impurities, the Pt₂Si growth continues unabated until the entire Pt film is reacted, at which time the initiation of the PtSi phase begins. However, it is apparent¹⁹ that a partial pressure of 10^{-7} Torr O₂ during the Pt evaporation may have incorporated sufficient O₂ to retard both the growth of Pt₂Si and PtSi as well as halt the growth of Pt₂Si before completion. Auger profiles have shown a significant accumulation of O₂ and Al contaminants at the Pt-Pt₂Si interface.^{18,20} It has been suggested that this accumulation may act as a barrier to the further growth of Pt₂Si.¹⁸ This would explain the oxygen partial pressure dependence observed by Crider.

The effect of a native oxide on Pt silicide is less well understood. It has been asserted that a sufficiently thick inter-

facial layer would act as a diffusion barrier to silicide formation.²¹ It was observed by Bower²² that an interfacial oxide grown in boiling H₂O₂ for 10 min was sufficient to completely prevent silicide formation with Cr and Mo, whereas little or no change was observed with Ti and Pd.

In the case of Pt, silicide formation occurs on air-exposed silicon surfaces even though such a surface appears ellipsometrically to have grown a thin SiO₂ layer. Recent work by Miller *et al.*²³ on the initial room temperature formation of Pd and Pt silicides showed that the metal still reacted with the air-exposed Si substrate, while O₂ remained on the metal. Subsequent Auger profiling showed no interfacial oxide, suggesting the SiO₂ had been reduced. However, a reduction of SiO₂ to form Pt₂Si is not thermodynamically favored and is not observed to occur on thick SiO₂ layers.²⁴

Results of the present study for Pt on clean, air exposed Si are shown in Figs. 1(a) and (b). Figure 1(a) illustrates a peak to peak Auger profile on an as-deposited sample while Fig. 1(b) is an identical sample heated for 1 h at 400°C under vacuum. From the splitting of the Si L_{VV} Auger peak (92 eV), it is apparent that the entire Pt film of the heated sample has reacted to form a mixed phase of platinum and di-platinum silicide (the exact stoichiometry is not known). The as-deposited film [Fig. 1(a)] appears to be partially reacted, possibly in part due to substrate heating during thermal evaporation of the Pt. It is of interest to note the presence of an oxygen layer at the Pt-silicide interface which is similar to that observed elsewhere.²⁰ Such a layer is present at the silicide sur-

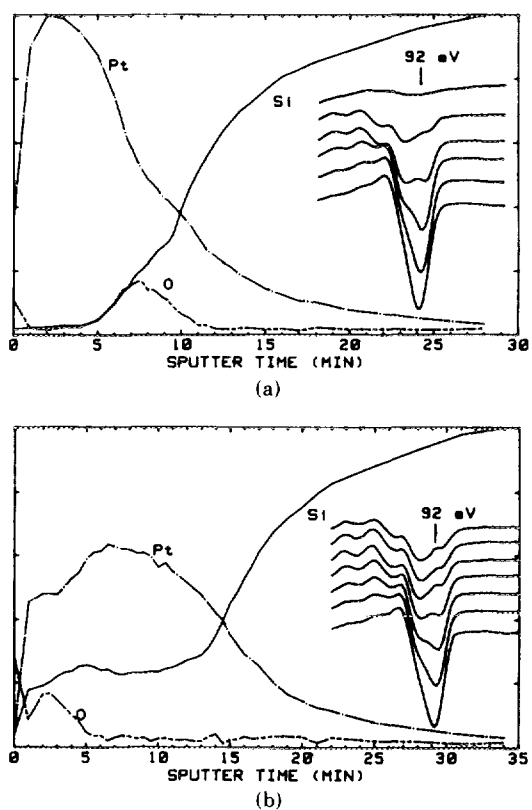


FIG. 1. (a) Peak-to-peak Auger sputter profile of Si 92 eV Auger lineshape for Pt deposited on room-temperature-oxidized Si, unheated. All profiles are from left to right. (b) Peak-to-peak Auger sputter profile and Si 92 eV Auger lineshape for Pt deposited on room-temperature-oxidized Si, heat treated at 400°C for 1 h in vacuum.

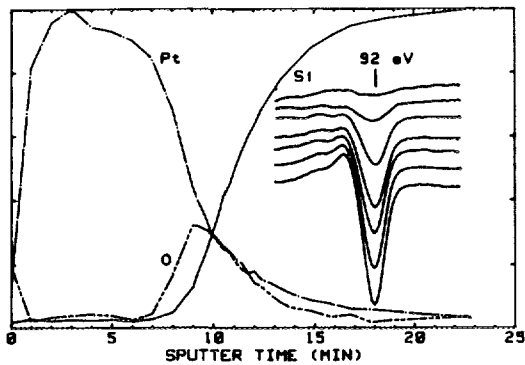


FIG. 2. Peak-to-peak Auger sputter profile and Si 92 eV Auger lineshape for Pt deposited on 30 Å thermally grown (700°C) SiO₂ on Si, heat treated at 400°C for 1 h in vacuum.

face in Fig 1(b), indicating that this moves with the Pt-silicide interface. The source of this oxygen pileup is believed to be oxygen incorporated in the Pt film during evaporation as well as the residual of the native oxide formed on the air exposed silicon. Ellipsometric measurements indicate that this native oxide is approximately 10 Å thick, although characterization of this layer as a stoichiometric SiO₂ film is probably invalid as will be discussed later.

The effect of a 30 Å SiO₂ layer on the interfacial reaction is shown in Fig. 2. As observed from the peak to peak profile and the Si 92 eV lineshape, 30 Å of SiO₂ is sufficient to completely prevent the formation of either Pt₂Si or PtSi at 400°C. Similar results were also found at 500°C. At 700°C, it appears that the Pt film agglomerated, complicating the interpretation of the Auger peak to peak profile. Thus, these profiles indicate that 30 Å of SiO₂ acts as an effective diffusion barrier to the formation of platinum silicide, while the native room temperature oxide which grows after etching acts as no barrier at all.

The chemical reduction of the air grown silicon oxide by Pt seems unlikely both on thermodynamic grounds as well as from Auger profiles of Pt on thick SiO₂ films which showed no reaction when heated. Previously, Miller *et al.*²³ have suggested an analogy between the Pd and Pt-SiO₂-Si systems and the reactive Au-SiO₂-Si^{13,14} system. However, the analogy, if it holds, does not appear to be a straightforward one. In the case of Au-SiO₂-Si, the Au-Si can form a liquid eutectic at 370°C which could plausibly dissolve SiO₂. However, the lowest eutectic temperature of the Pt-Si binary alloy is 830°C, as distinguished from the 400°C of the present experiments and the room temperature experiments of Miller *et al.* Therefore alloy formation and subsequent SiO₂ dissolution appears unlikely in the case of Pt at low temperatures.

An alternate explanation considers the nature of room temperature air grown oxide to be different from that of the thermally grown oxide. Several reports indicate that the initial room temperature oxide on Si can not be represented as silicon dioxide but rather as a primarily adsorbed layer of O₂.^{25,26} This layer has been observed to form Si-O bonds when excitation such as ion or electron bombardment is provided.^{15,25} If the air grown oxides were not fully formed, the deposition of a metal on this layer could easily break the adsorption bond and allow intimate contact with the Si substrate. Further

J. Vac. Sci. Technol., Vol. 18, No. 3, April 1981

studies using oxide thicknesses intermediate to those studied here would be useful in resolving this phenomenon.

B. Au-Si

The Au-Si contact is characterized by interdiffusion occurring at the Au-Si interface.^{8,27} At low temperature, diffusion of elemental Si into the Au film is quite rapid, so rapid in fact that samples kept at room temperature will show discoloration after several days due to the appearance of Si on the gold surface.²⁸ Interdiffusion is evident even at liquid nitrogen temperatures.²⁹

Although gold does not appear to form a stable bulk compound with Si, the existence of a thin metastable phase of Au and Si is frequently observed.¹⁰⁻¹² This phase is typically evidenced by a splitting of the 92 eV Si peak into peaks located at 88.5 and 95 eV.¹⁰ The thickness of this layer is on the order of 25-50 Å and has been shown by LEED studies to form a crystalline phase when annealed.³⁰

Alessandrini *et al.*^{13,14} have studied the interaction of Au on SiO₂ under heat treatment temperatures ranging from 500° to 700°C. They suggest that the Au does not reduce the SiO₂, since this is not thermodynamically favorable. As discussed by Alessandrini, a more likely mechanism is the diffusion of Au through the SiO₂ to form a liquid Au-Si alloy which then may dissolve the SiO₂ film.

In the present study, both Auger and XPS depth profiling were performed on as-deposited, unoxidized Au-Si samples. Interdiffusion was found to be prevalent at the interface, with the characteristic splitting of the 92 eV Si peak shown in Fig. 3 being observed. The interdiffusion of Si into the Au film at room temperature was observed to occur continuously, as evidenced by increasing discoloration of the Au with time. Auger profiling of samples after several months on the shelf indicated the growth of an SiO₂ layer on the surface of the Au and extensive interdiffusion throughout the sample. In the region of greatest mixing, XPS revealed a 0.9 eV shift in the Au 4f 7/2 line to higher binding energy, coupled with a 0.4 eV shift in the Si 2p peak, also to higher energy. This is similar to observations by Abbati.²⁹ Such spectra are suggestive of

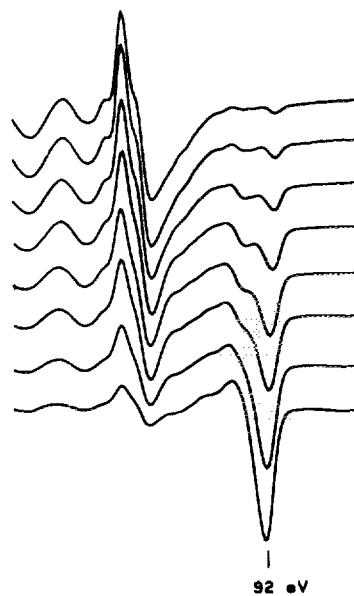
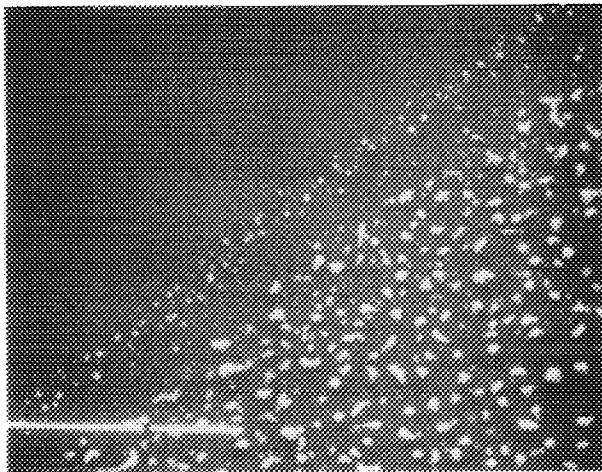


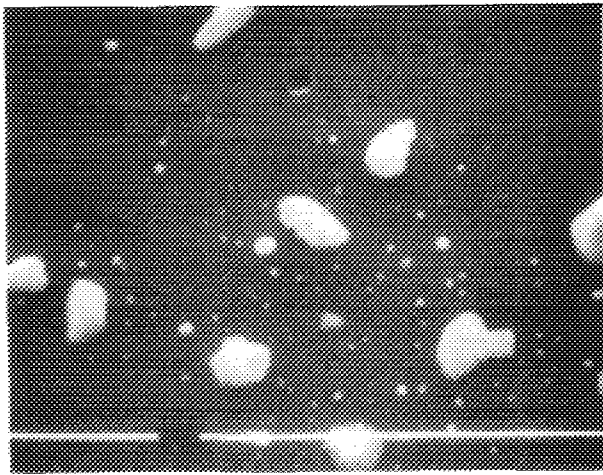
FIG. 3. Si LVV Auger lineshape at Au-Si interface, unheated.

chemical bonding, although matrix effects may also induce a shift in XPS peaks.³¹ Heat treatment of air exposed samples at 400°C resulted in severe agglomeration of the gold film as shown in the SEM micrograph of Fig. 4(a). Increased magnification, Fig. 4(b), indicated the presence of etch pits, which probably resulted from Si dissolution into the Au upon heating above the eutectic temperature. Auger profiles after heat treatment showed no evidence of a silicide phase, although interpretation of the profiles was difficult due to the topological effects of agglomeration.

The presence of 30 Å thermally grown interfacial oxide appears to prevent the Au-Si interface reaction and interdiffusion previously seen, even after heat treatment at 400°C for 1 h. No evidence of splitting in the 92 eV Si Auger peak was observed, and the Auger profile after heat treatment is almost identical to profiles on unheated samples, as shown in Fig. 5. Here the least squares mixing technique described earlier was used to establish the presence of interfacial SiO₂. SEM studies (Fig. 6) indicated that at least a limited reaction occurred for a heat treated sample. Unheated samples presented few topological features, whereas Fig. 6 shows a certain amount of agglomeration occurring. X-ray dispersion measurements demonstrated that the bright areas are indeed agglomerated Au while the background is still a thin gold



(a)



(b)

FIG. 4. (a) SEM micrograph, 2100X, at the edge of the Au-Si (room temperature oxide) contact after heat treatment at 400°C for 1 h in vacuum. (b) Same sample as Fig. 4(a), 10 500X, showing etch pits.

J. Vac. Sci. Technol., Vol. 18, No. 3, April 1981

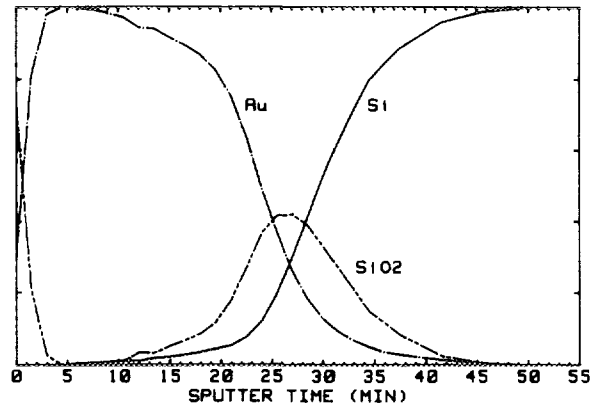


FIG. 5. Auger sputter profile for Au-30 Å SiO₂-Si generated using a least squares fit of pure Au, Si, and SiO₂ Auger lines.

layer. The agglomeration observed on the thin SiO₂ layer is however not nearly as extensive as what was detected with the unoxidized case. This may indicate a decrease of the Si-Au interfacial energy due to the presence of the thin SiO₂ layer.

Heat treatment of oxidized samples at 500°C showed a much more severe reaction. This may be seen in the SEM photo and Auger surface scan of Fig. 7. The strong 92 eV Si peak indicates that the bare areas are in this case exposed Si.

We believe that the reaction observed at 500°C is similar to that observed by Alessandrini *et al.*^{13,14} on thick SiO₂ layers, i.e., the SiO₂ layer has been dissolved by the Au-Si alloy at 500°C. The limited reaction observed at 400°C indicates that the heat treatment was carried out long enough for the Au to penetrate the SiO₂, although not in sufficient quantities to be detected by Auger profiling. The sample is apparently in the initial stages of the reaction observed at higher temperatures and given enough time, it would probably also completely dissolve the interfacial layer.

C. Al-SiO₂-Si

The dissolution of Si by Al films has long been a problem in integrated circuit technology.³² The diffusion of Si through

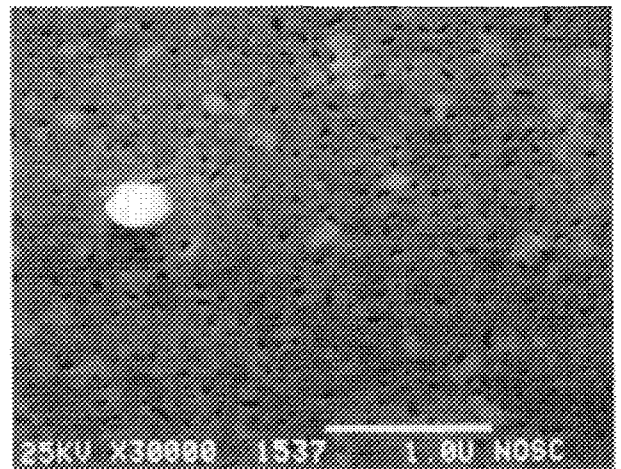


FIG. 6. SEM photo, 30 000X, of sample shown in Fig. 5 (prior to profiling).

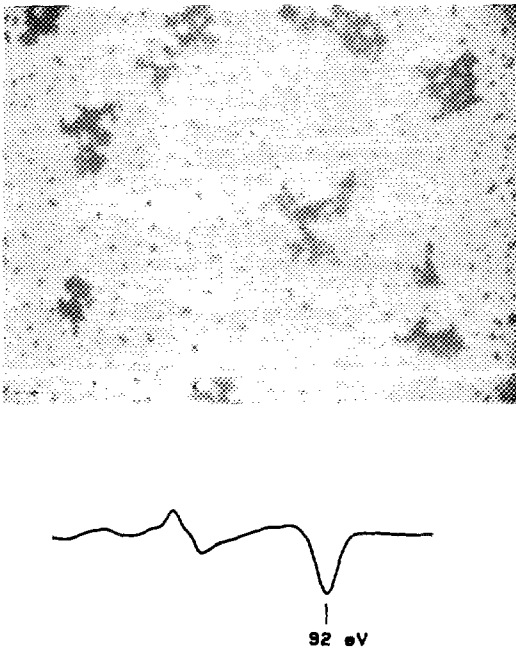


FIG 7. SEM photo, 13 500X, for Au-30 Å SiO₂-Si heated for 1 h at 500° in vacuum, including Auger line after 1 min sputtering.

Al is found to be very rapid at low temperature, similar to Si in Au.⁸ Upon heating above 150°C, Si is readily dissolved and diffuses throughout the Al film. Subsequent cooling results in Si precipitation from the Al both at the interface and the Al surface.³³

As mentioned earlier, it is thermodynamically favorable for Al to reduce SiO₂ to form Al₂O₃. This reaction has been observed by Strausser³⁴ and others using Auger profiling of Al-SiO₂ structures. Al₂O₃ and free Si were detected at the interface of the Al-SiO₂ indicating a reduction had occurred. Olsen *et al.*³⁵ have observed the reaction on thin SiO₂ layers (23 Å) where it appeared that the entire SiO₂ film was reduced to form Al₂O₃. Bauer *et al.*³⁶ have studied the reduction of SiO₂ by Al in detail using photoemission to show that the Al forms an intermediate oxidation state prior to forming Al₂O₃.

Results in the present study are in general agreement with the previous results. Figure 8(a) shows the peak-to-peak profile of an unheated sample with an air grown oxide. It appears that Si has diffused into the Al and collected at the Al₂O₃-Al interface at the surface. No buildup of Al₂O₃ is seen at the Al-Si interface. Figure 8(b) is a profile of an unheated sample with 30 Å SiO₂ at the interface. In contrast to the air exposed sample, an Al₂O₃ layer exists at the Al-SiO₂-Si interface. This is suggestive of the reduction reaction seen previously,³⁴ with the presence of SiO₂ necessary for formation of Al₂O₃. Heat treatment of samples resulted in little change in the profiles with the exception of greater concentration of Si at the surface of the unoxidized samples.

Attempts to resolve SiO₂ from the LVV Auger spectra using the least squares fitting technique met with only limited success, perhaps due to background problems. XPS depth profiling was instead employed to ascertain the extent of SiO₂ reduction. The results indicated that both SiO₂ and Al₂O₃ existed simultaneously at the interface, implying that the

reaction is self-limiting, even at elevated temperatures. This is probably a result of the diffusion barrier formed by the Al₂O₃ layer to the transport of Al to the SiO₂ layer.

IV. CONCLUSIONS

The effect of a thin SiO₂ layer on metal-silicon contact formation has been investigated here for Pt, Au, and Al on (100) Si. The 30 Å thermally grown SiO₂ layer appears as a complete barrier to the formation of platinum silicide at both 400° and 500°C after 1 h. In contrast, chemically etched surfaces were transparent to the growth of platinum silicide. The same SiO₂ layer presented less of a barrier to the Au-Si reaction than in the Pt case. At 400°C, SEM micrographs indicated a limited reaction, while at 500°C, widespread dissolution of the SiO₂ layer and reaction between the Au and Si appeared to occur. This is interpreted as a result of Au diffusion into the Si to form a Au-Si eutectic which attacked the SiO₂ layer. As is seen in other studies, Al partially reduces the thin SiO₂ layer to form Al₂O₃ and free Si. This reaction appeared to be self limiting, with SiO₂ still present at the interface, even after heating at 400°C.

In conclusion, a thermally grown SiO₂ layer appears effective in preventing or retarding the widespread interdiffusion of elemental Si. However, chemically etched surfaces react readily with the metal overlayer even though a thin native oxide grows prior to deposition. The different chemical nature of room temperature air grown oxides of Si is suggested as an explanation of these results.

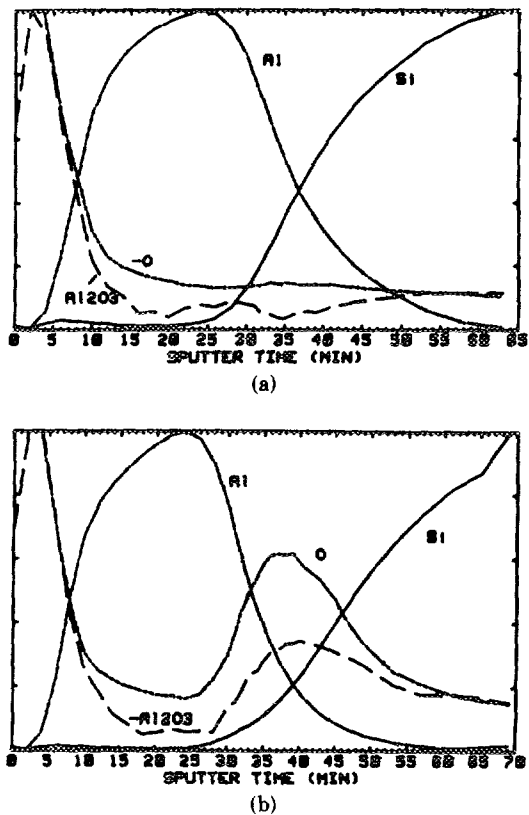


FIG 8. (a) Peak-to-peak Auger sputter profile of Al on room temperature oxidized Si, unheated. (b) Peak-to-peak Auger sputter profile of Al on 30 Å SiO₂, unheated.

ACKNOWLEDGMENTS

The authors wish to acknowledge the SEM and x-ray dispersive work of Neil Davis of NOSC. This work was supported in part by ONR.

- ¹M. J. Turner and E. H. Rhoderick, *Solid State Electron.* **11**, 291, (1968).
²J. C. Phillips, *Phys. Rev. Lett.* **35**, 56 (1975).
³A. M. Cowley and S. M. Sze, *J. Appl. Phys.* **36**, 3212 (1965).
⁴S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, *J. Vac. Sci. Technol.* **13**, 790 (1976).
⁵J. Bardeen, *Phys. Rev.* **71**, 717 (1947).
⁶G. Margaritondo, J. E. Rowe, and S. B. Christman, *Phys. Rev. B* **14**, 5396 (1976).
⁷J. C. Phillips, *J. Vac. Sci. Technol.* **11**, 947 (1974).
⁸J. O. McCaldin, *J. Vac. Sci. Technol.* **11**, 990 (1979).
⁹P. V. Gray, *Phys. Rev. A* **140**, 179 (1965).
¹⁰T. Narusawa, S. Komiya, and A. Hiraki, *Appl. Phys. Lett.* **22**, 389 (1973).
¹¹A. K. Green and E. Bauer, *J. Appl. Phys.* **47**, 1284 (1976).
¹²K. Okuno, T. Ito, M. Iwami, and A. Hiraki, *Solid State Commun.* **34**, 493 (1980).
¹³E. I. Alessandrini, D. R. Campbell, and K. N. Tu, *J. Appl. Phys.* **48**, 4888 (1974).
¹⁴E. I. Alessandrini, D. R. Campbell, and K. N. Tu, *J. Vac. Sci. Technol.* **13**, 55 (1976).
¹⁵D. L. Ellsworth and C. W. Wilmsen, *Proceedings of the Conference on the Physics of MOS Insulators*, edited by G. Lucovsky, S. T. Pantetides, and F. L. Galeener (Pergamon, New York, 1980).
¹⁶K. N. Tu, *Appl. Phys. Lett.* **27**, 221 (1975).
¹⁷J. M. Poate and T. C. Tisone, *Appl. Phys. Lett.* **24**, 391, (1980).
¹⁸C. Canali, C. Catallani, and M. Prudenziati, *Appl. Phys. Lett.* **31**, 43 (1977).
¹⁹C. A. Crider and J. M. Poate, *Appl. Phys. Lett.* **36**, 417 (1980).
²⁰B. Bindell, J. W. Colby, D. R. Wonsidler, J. M. Poate, D. K. Conley, and T. C. Tisone, *Thin Solid Films* **37**, 441 (1976).
²¹K. N. Tu and J. W. Mayer, in *Thin Films Interdiffusion and Reaction*, edited by J. M. Poate, K. N. Tu, and J. W. Mayer (Wiley, New York, 1977), Chap. 10.
²²R. W. Bower and J. W. Mayer, *Appl. Phys. Lett.* **20**, 359 (1972).
²³J. N. Miller, S. A. Schwarz, I. Lindau, W. E. Spicer, B. DeMichelis, I. Abbati, and L. Braicovich, *J. Vac. Sci. Technol.* **17**, 920 (1980).
²⁴R. Pretorius, J. M. Harris, and M. A. Nicolet, *Solid State Electron.* **21**, 667 (1978).
²⁵S. I. Raider, R. Flitsch, and M. J. Palmer, *J. Electrochem. Soc., Solid State Sci.* **122**, 413 (1975).
²⁶H. Ibach and J. E. Rowe, *Phys. Rev. B* **9**, 1951 (1974).
²⁷A. Hiraki, M. A. Nicolet, and J. W. Mayer, *Appl. Phys. Lett.* **18**, 178 (1971).
²⁸K. Nakashima, M. Iwami, and A. Hiraki, *Thin Solid Films* **25**, 423 (1975).
²⁹I. Abbati, L. Braicovich, A. Franciosi, I. Lindau, P. R. Skeath, C. Y. Su, and W. E. Spicer, *J. Vac. Sci. Technol.* **17**, 930 (1980).
³⁰H. L. Gaigher and N. G. Van der Berg, *Thin Solid Films* **68**, 373 (1980).
³¹K. S. Kim and N. Winograd, *Chem. Phys. Lett.* **30**, 91 (1975).
³²C. J. Kircher, *J. Appl. Phys.* **47**, 5394 (1976).
³³G. J. van Gorp, *J. Appl. Phys.* **44**, 2040 (1973).
³⁴Y. E. Strausser and K. J. Majumder, *J. Vac. Sci. Technol.* **15**, 238 (1978).
³⁵L. C. Olsen, D. L. Barton, W. Miller, J. E. Garnier, and R. P. Turcotti, *Proc. 15th IEEE Photovoltaics Spec. Conf.*, San Diego, 1980.
³⁶R. S. Bauer, R. Z. Bachrach, and L. J. Brillson, *Proceedings of the Conference on the Physics of MOS Insulators*, edited by G. Lucovsky, S. T. Pantetides, and F. L. Galeener (Pergamon, New York, 1980).