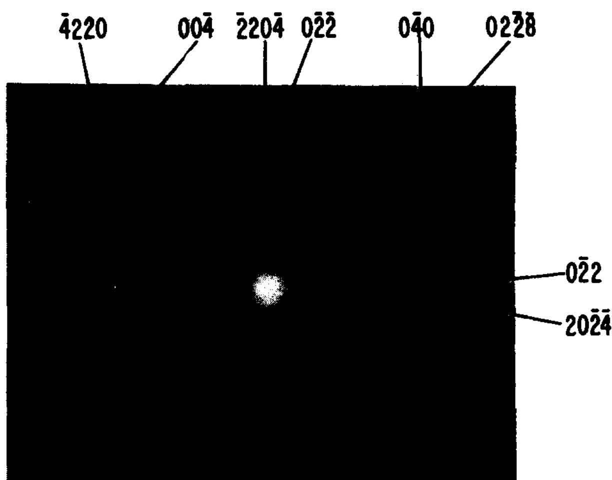

FIG. 2. Diffraction pattern of $100_{Si}/01\bar{1}2_{Al_2O_3}$ corresponding to Fig. 1. Three and four symbol indices refer to Si and Al_2O_3, respectively. Note that the original SOS growth interface is retained in this sample.

0.5 and 3.5 sec. In the 0.5-sec sample, the diffracted intensity from the Si islands was too weak to be usable. In the 3.5-sec sample, the coverage of the sapphire by Si was about 90% complete, and fringes associated with defects in the Si, such as stacking faults and microtwins,[6,7,9] interfered with our observations.

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[1]E. J. Boleky and J. E. Meyer, IEEE J. Solid State Circuits SC-7, 135 (1972).
[2]A. C. Ipri and J. C. Sarace, 1974 IEEE International Solid State Circuits Conference, Digest of Technical Papers, Paper No. WPM6.3, p. 58 (unpublished).
[3]T. S. LaChapelle, A. Miller, and F. L. Morritz, in *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon, London, 1967), Vol. 3.
[4]C. Y. Ang and H. M. Manasevit, Solid-State Electron. **8**, 994 (1965).
[5]See, for instance, G. W. Cullen, J. Cryst. Growth **9**, 107 (1971).
[6]R. W. Bicknell, B. A. Joyce, J. H. Neave, and G. V. Smith, Philos. Mag. **14**, 31 (1966).
[7]A. G. Cullis, Ph.D. thesis (Oxford University, Oxford, England, 1972) (unpublished).
[8]S. T. Picraux and G. J. Thomas, J. Appl. Phys. **44**, 594 (1973).
[9]P. F. Linnington, Ph.D. thesis (Cambridge University, Cambridge, England, 1974) (unpublished).
[10]M. S. Abrahams and C. J. Buiocchi, Appl. Phys. Lett. **27**, 324 (1975).
[11]M. S. Abrahams, C. J. Buiocchi, and M. D. Coutts, Rev. Sci. Instrum. **39**, 1944 (1968).
[12]P. B. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley, and M. J. Whelan, *Electron Microscopy of Thin Crystals* (Butterworth, Washington, D.C., 1965), p. 247.
[13]J. Hornstra, J. Phys. Chem. Solids **5**, 129 (1958).
[14]Reference 12, p. 358.
[15]F. C. Frank and J. H. van der Merwe, Proc. R. Soc. London A **198**, 216 (1948).

Ti and V layers retard interaction between Al films and polycrystalline Si†

K. Nakamura,* S. S. Lau, M-A. Nicolet, and J. W. Mayer

California Institute of Technology, Pasadena, California 91125

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Fine-grained polycrystalline Si (poly Si) in contact with Al films recrystallizes at temperatures well below the Si-Al eutectic (577 °C). We show that this interaction can be deferred or suppressed by placing a buffer layer of Ti or V between the Al film and the poly Si. During annealing, Ti or V form $TiAl_3$ or VAl_3 at the buffer-layer–Al-film interface, but do not react with the poly Si, so that the integrity of the poly Si is preserved as long as some unreacted Ti or V remains. The reaction between the Ti or V layer and the Al film is transport limited ($\propto t^{1/2}$) and characterized by the diffusion constants $1.5\times10^{15}\exp(-1.8\,eV/kT)$ Å^2/sec or $8.4\times10^{12}\exp(-1.7\,eV/kT)$ Å^2/sec, respectively.

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Polycrystalline Si (poly Si) is used extensively in integrated circuits for gates of MOS's or as an intermediate layer between an Al metallization and the single-crystal substrate to prevent dissolution of the Si substrate into the Al metallization.[1] In a previous investigation, we found that the Al layers in contact with poly Si induce migration and recrystallization of the Si at temperatures, (e.g., 400 °C) well below the eutectic point of Si and Al (577 °C).[2]

Bower has shown that the dissolution of a single-crystal Si substrate can be deferred by placing a Ti film between the Al layer and the Si substrate.[3] In this letter, we report a similar method applied to delay the recrystallization of poly Si induced by an Al layer. The concept is as follows: when an Al metallization is deposited on poly Si, the integrity of the poly Si substrate can be prolonged by separating the top Al film from the substrate with an intermediate buffer layer. During

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subsequent annealing, this buffer layer should react only with the Al film by forming a laterally uniform compound at the buffer-Al interface. As long as this reaction does not fully consume the buffer layer, separation between the substrate and the Al is maintained. Since, by assumption, the buffer layer does not react with the poly Si, the integrity of the poly Si substrate is preserved. In this study, the silicide-forming refractory metals Ti and V were chosen for the buffer layer because on single-crystal Si substrates, films of these metals begin to form a silicide only above 550 °C.[3-7]

A layer of 500–2500 Å of Ti or V was vacuum evaporated on 3000–5000 Å of poly Si. The poly Si had been chemically deposited at 640 °C on a Si wafer covered with 1000 Å of SiO_2. Then, a 1500–12000-Å film of Al was vacuum evaporated on top of the Ti or V layer. Both evaporations were performed consecutively without breaking vacuum, with an electron gun, at a pressure below 5×10^{-7} Torr. Other samples in which one of the two metal evaporations was omitted were also made. The annealing was performed in a vacuum furnace at a pressure below 10^{-6} Torr and temperatures between 450 and 550 °C. MeV ^{4}He backscattering spectrometry, scanning electron microscopy, electron microprobe, and x-ray diffraction techniques were employed in the analysis.

An example of recrystallization of poly Si in direct contact with Al induced by annealing for 30 min at 450 °C is shown in Fig. 1(a). The SEM micrograph was taken after the Al film had been chemically removed. The picture reveals micrometer-sized grains imbedded in the Al matrix. These grains are Si crystallites.[2] Most of the original fine-grain poly Si is seen to have been converted into big distinct crystallites.

A sample with a buffer layer of 1300 Å of Ti inserted between a 2900-Å film of Al and the poly Si substrate was annealed at 450 °C for 1 h. The transformation which took place during annealing is revealed in the backscattering spectra taken before and after annealing and is shown in Fig. 2. After annealing, steps on the high-energy side of the Ti signal and on low-energy side of the Al signal clearly indicate that Al and Ti have reacted. The amplitude ratio of the two steps gives the atomic concentration ratio in this layer, which is found to be approximately Ti:Al = 1:3. This agrees with the results of Bower, who reports that double layers of Ti and Al form $TiAl_3$ upon annealing.[3] On the other hand, no change is observed in the low-energy portion of the Ti signal or in the signal of poly Si; therefore, poly Si and Ti did not react.

The sample shown in Fig. 2(b) was also etched for SEM observation. First, the remaining Al film on the surface was removed with a H_3PO_4 etch,[8] then the $TiAl_3$ and Ti layers were etched away with diluted HF to reveal the poly Si surface. An SEM micrograph of this surface is shown in Fig. 1(b). The surface looks very smooth compared with that shown in Fig. 1(a), confirming that there was no significant recrystallization of the poly Si. The thickness of the poly Si on this sample was measured by backscattering analysis and found to be unchanged, which provides further evidence that the surface observed in Fig. 1(b) is the original poly Si surface.

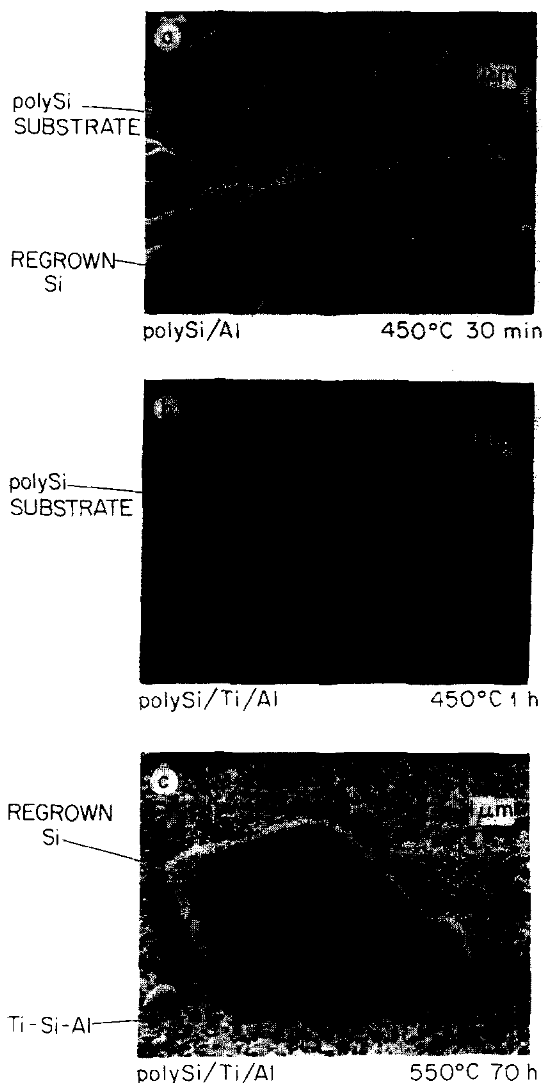

FIG. 1. Scanning electron micrographs of various samples after chemical etching. (a) A sample of poly Si (0.5 μm) covered with Al (1.2 μm), annealed at 450°C for 30 min, and after the Al was etched away with H_3PO_4. (b) A sample of poly Si (0.45 μm) with a barrier layer of Ti (1300 Å) under the Al (2900 Å), annealed at 450°C for 1 h, and after the Al was etched away first with H_3PO_4, then the $TiAl_3$ and the Ti layers were etched away with HF. (c) A sample of poly Si (0.5 μm) with a barrier layer of Ti (500 Å) under the Al (1.2 μm), annealed at 550°C for 70 h, and after the Al was etched away with H_3PO_4. The incident angle of the electron beam with respect to the normal of the sample is 60° in each case.

If there is less Ti in the buffer layer than is required to convert all the Al to $TiAl_3$, the integrity of the poly Si-Ti interface is lost after all the Ti layer is consumed. Backscattering analysis shows that once the $TiAl_3$ layer reaches the poly Si surface, Si migrates into the $TiAl_3$ layer to form a Ti-Si-Al ternary compound.[3] After prolonged annealing, Si migrates through this compound layer into the remaining Al and again forms crystallites. Figure 1(c) shows a SEM picture of such a crystallite. Electron microprobe analysis confirms that these crystallites consist of almost pure Si and some oxygen. To preserve the integrity of the poly Si substrate, it is therefore necessary that some unreacted Ti remain after annealing. Allowable annealing

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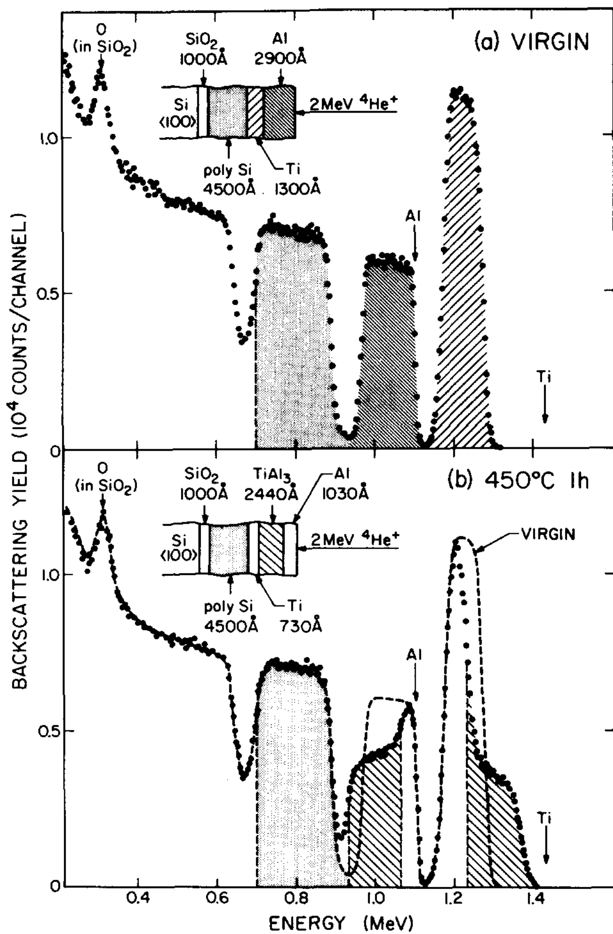

FIG. 2. Backscattering spectra of samples of poly Si (4500 Å)/Ti (1300 Å)/Al (2900 Å): (a) Before annealing and (b) after annealing at 450 °C for 1 h. The arrows incidate the energy corresponding to scattering from atoms at the surface.

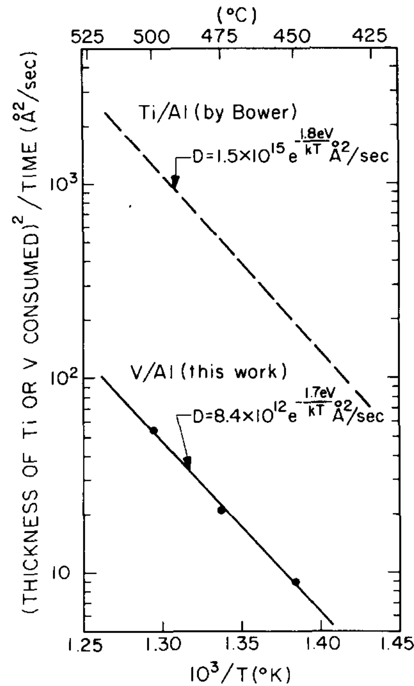

FIG. 3. Arrhenius plot of the rate of consumption of Ti or V in the reaction with Al for the formation of $TiAl_3$ (Ref. 3) or VAl_3.

times and temperatures can be obtained from the kinetics data of the reaction $Ti + 3Al \rightarrow TiAl_3$ given by Bower and reproduced in Fig. 3.[3]

If the Ti layer is thick enough, all the Al can be converted to $TiAl_3$ without fully depleting the Ti. Backscattering spectra show that when this is the case no further reactions or dissolutions of the poly Si occur at 450 °C for annealing times up to 10 h.

The characteristics of V as a buffer layer are quite similar to those of Ti. No silicide forms between V and poly Si after annealing at temperatures up to 500 °C for 15 h. On the other hand, V reacts with Al during annealing. X-ray diffraction analysis identifies the reaction product as VAl_3. We have also determined the rate of VAl_3 formation in the temperature range between 450 and 500 °C. The amount of V consumed in the reaction with Al increases proportionally to $t^{1/2}$, as in the case of Ti and Al. The activation energy for the growth of VAl_3 is about 1.7 eV (Fig. 3). After all V is consumed, the reaction proceeds as in the case of Ti and Al [Fig. 1(c)] i.e., there is a loss of poly Si and formation of Si crystallites in the remaining Al. Compared to Ti, V reacts roughly 20 times slower with Al (see Fig. 3). The same protective effect is thus obtained with much thinner V buffer layers than with Ti.

It is worth noting that the activation energies for growth for $TiAl_3$ and VAl_3 are nearly the same (1.8 and 1.7 eV, respectively), but the preexponential constants are different by a factor of about 200. The reason for this is not clear at present; different structures in the compounds (i.e., grain size, etc.) could have an effect on the preexponential factor.

In summary, the recrystallization of poly Si in contact with Al films can be prevented by interposing a buffer layer such as Ti or V between poly Si and Al. This layer effectively acts as a barrier as long as not all the Ti or V is consumed in the reaction with Al. If all Ti or V is consumed, poly Si migrates through the intermediate layer and again forms crystallites in the top remaining Al layer.

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*Permanent address: Nippon Electric Co., Ltd., IC Division, Kawasaki, Japan.
[1]S. P. Bellier and L. B. Ehlert, *Semiconductor Silicon* 1973, edited by H.R. Huff and R.R. Burgess (The Electrochemical Society, Inc., Princeton, 1973), p. 304.
[2]K. Nakamura, M-A. Nicolet, J.W. Mayer, R.J. Blattner, and C.A. Evans, Jr., J. Appl. Phys. **46**, 4678 (1975).
[3]R.W. Bower, Appl. Phys. Lett. **23**, 99 (1973).
[4]R.W. Bower and J.W. Mayer, Appl. Phys. Lett. **20**, 359 (1972).

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[5]H. Krautle, W.K. Chu, M-A. Nicolet, J.W. Mayer, and K.N. Tu, *Application of Ion Beams to Metals*, edited by S.T. Picraux, E.P. EerNisse, and F.L. Vook (Plenum, New York, 1974), p. 193.
[6]K.N. Tu, J.F. Ziegler, and C.J. Kircher, Appl. Phys. Lett. 23, 493 (1973).
[7]H. Krautle, M-A. Nicolet and J.W. Mayer, J. Appl. Phys. 45, 3304 (1974).
[8]It has been found that Al surface layer can be selectively removed in a chemical etchant, consisting of 40 parts H_3PO_4, 2 parts HNO_3, and 9 parts H_2O. At room temperature, this etchant removes approximately 1000 Å of Al per min and less than 50 Å of $TiAl_3$ in the same period of time.

Changes in Au-GaAs Schottky barrier diodes with low neutron fluence*

J. M. Borrego and R. J. Gutmann

Electrical and Systems Engineering Department, Rensselaer Polytechnic Institute, Troy, New York 12181
(Received 13 October 1975)

Guarded Au/n-GaAs Schottky barrier diodes fabricated from epitaxial and bulk material with carrier concentrations of 2.2×10^{16} and 7.8×10^{16} cm^{-3}, respectively, were exposed to fast neutron fluences between 3.6×10^{14} and 2.2×10^{15} neutron/cm^2. The forward I-V and 1-MHz C-V characteristics remained relatively unchanged after irradiation at the lower fluences where carrier compensation is small (reduction in carrier concentration less than 15%). However, the reverse current increased by more than one order of magnitude at room temperature, which is neither a result of surface leakage (prevented by the guarded device structures used), classical generation-recombination current (depletion volume changes are too small), nor thermionic emission (too weak a temperature dependence). This increase in reverse current is attributed to enhanced field emission from traps.

PACS numbers: 85.30.H, 73.30., 61.80.H, 73.40.E

Previous work has indicated that the principal effects of radiation damage in Schottky barrier diodes are caused by reduced effective carrier concentration, mobility degradation, and reduced lifetime.[1-4] As a result of the reduction in these material parameters, the following changes take place in diode characteristics: the reverse current density increases, the ideality factor (or n factor) increases, the capacitance decreases (for fixed voltage), and the series resistance increases. In this letter we report on fast neutron effects in Au/n-GaAs Schottky barrier diodes at low fluences, defined as fluences below which carrier removal effects dominate diode characteristics. An increase in reverse leakage current occurs at low neutron fluences which cannot be accounted for by the principal effects described above. Enhanced field emission from traps is believed to be a principal cause of this reverse current.

The Au/n-GaAs Schottky diodes were fabricated using conventional processing techniques. A guarded structure,[5] consisting of a 15-mil-diam device (approximately 10^{-3} cm^2) and a 3-mil-wide guard ring separated by 1 mil from the device, was used to prevent surface currents from affecting I-V measurements. Automated swept dc I-V and 1-MHz C-V measurements were taken from 77 to 400°K before and after radiation. Typical room-temperature characteristics obtained with two series of devices prior to irradiation are given in Table I.

The neutron irradiations were performed on the water-moderated Biomedical Research Reactor (BMRR) at the Brookhaven National Laboratory. At the 100-kw operating power used, the fast neutron flux is 0.6×10^{12} neutrons/cm^2/sec. The time of irradiation was varied from 10 to 60 min in obtaining a fluence from 3.6×10^{14} to 2.2×10^{15} neutron/cm^2.

The I-V characteristics before and after irradiation are shown in Fig. 1 for series 2E16. From this data we can conclude that the n factor remains relatively constant (increases from 1.01 to 1.05), any increase in series resistance has a negligible effect (log$I$ vs V remains linear under forward bias to at least 1 mA, although this range is not shown), and the reverse current increases by over one order of magnitude at 24°C (with

TABLE I. Room temperature characteristics of Au/n-GaAs Schottky diodes.

Device Series	Starting material	Carrier concentration (cm^{-3})	n factor (taken over 10^{-9}–10^{-7} A)	Saturation current (A) (extrapolated from I-V data)	Reverse current (A) at 4 V
2E16	Epitaxial [VPE(100)]	2.2×10^{16}	1.01	6×10^{-12}	4×10^{-11}
316	Bulk [boat grown (100)]	7.8×10^{16}	1.05	3×10^{-11}	2×10^{-9}

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