TABLE III. Pt/W/Pt No. 1 rf performance data.

Diode	dc input			rf output		
	I	V	P (W)	P (mW)	f (GHz)	Eff. (%)
1	300	97.6	29.2	2800	5.8	9.6
2	390	108.6	38.0	3782	5.9	9.9
3	390	99.7	34.9	3780	5.7	10.8
4	430	101.8	40.7	4700	5.9	11.5

a change[4] in the rf performance of high-efficiency devices over their expected lifetimes (10^5 h) and therefore must be eliminated. It appears that this sandwich contact does eliminate aging due to contact chew in.

The author is grateful to J.C. Irvin and S.M. Sze for many helpful discussions. Also, to E. Heinlein for depositing the sandwich-structure metallizations and to A. Sinha and T. Smith for the platinum depositions.

[1]J.C. Irvin, *Proceedings of the Fourth* (1973) *Biennial Cornell Electrical Engineering Conference* (Cornell U.P., Ithaca, N.Y., 1973), pp. 287–298.
[2]A.K. Sinha and J. Poate, Appl. Phys. Lett. **23**, 666 (1973); also, Jpn. J. Appl. Phys. (to be published).
[3]D.J. Coleman Jr., W.R. Wisseman, and D.W. Shaw, Appl. Phys. Lett. **24**, 355 (1974).
[4]W.C. Niehaus and P.F. Sciortino, Solid-State Electron. (to be published).
[5]A.K. Sinha, Appl. Phys. Lett. **26**, 171 (1975).

Oxide thickness dependence of electron-induced surface states in MOS structures

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(Received 17 June 1975; in final form 2 September 1975)

To gain insight into the origin of the surface states induced by electron radiation, MOS structures with different oxide thicknesses were irradiated with a 25-keV electron beam. For a dose of 0.95×10^{-5} C/cm^2, the surface states increased monotonically as the oxide thickness increased from 90 to 2100 Å. Since all the oxides were grown under the same oxidation conditions and their initial surface states were of the same density, the results could not be due to the difference in their interface properties. The experimental results can be explained by a postulation based on a broken-bond model.

PACS numbers: 73.40.Q, 73.20., 79.20.K

It is known that energetic electron radiation can generate electronic surface states at the Si-SiO_2 interface in MOS structures.[1–4] The energy distribution of the surface states so generated has been reported previously for n- and p-type silicon substrates with doping in various concentrations.[5] Two models have been proposed to explain the mechanisms that cause these electron-induced surface states. The first, called the broken-bond model, suggests that the electron beam breaks the initially strained bonds in the SiO_2, leading to structural modifications of the insulating film. The resulting shrinkage of the film causes many of the bonds at the Si-SiO_2 interface to break, and these broken bonds in turn act as new surface states.[2,6] The second model, called the hydrogen model, suggests that a hydrogen-related center at the initial Si-SiO_2 interface captures an incident electron, which breaks the bond between the hydrogen and the center, permitting the hydrogen to escape; thus a surface state is formed.[4,7]

Although it is not clear at present which model has more merit, our recent data favor the broken-bond model.[5,8] To gather further evidence, an experiment inspired by the results described in Ref. 8 was designed.[9] In the experiment, the surface states induced by the electron radiation in MOS capacitors having different oxide thicknesses were measured. Although all the oxides were grown under the same temperature and oxygen conditions, the radiation-induced surface-state density was found to increase monotonically as oxide thickness increased from 90 to 2100 Å. These results, consistent with those found earlier,[8,9] further support the broken-bond model and cannot be explained by the hydrogen model.

The MOS capacitors were fabricated as follows. Silicon wafers with ⟨100⟩ orientation, boron doping, and a resistivity of about 2 Ω cm were first chemically cleaned. They were then oxidized in dry oxygen at 1000 °C for different lengths of time to obtain thermal oxides 90, 160, 260, 730, and 2100 Å thick. After the oxidation, the wafers were left in the 1000 °C furnace and annealed in dry N_2 for 30 min. They were then withdrawn slowly, placed in a covered container to minimize contamination, and transferred to an evaporator for aluminum metallization. Approximately 4000 Å of pure Al was evaporated through a stainless-steel mask onto the front side of each wafer by use of a heated Ta boat, to produce a 10×10 array of dots 20 mil in diameter. The back was stripped of oxide and then metallized. No further annealing was done after the metallization. The maximum temperature encountered by the wafer after withdrawl from the furnace is esti-

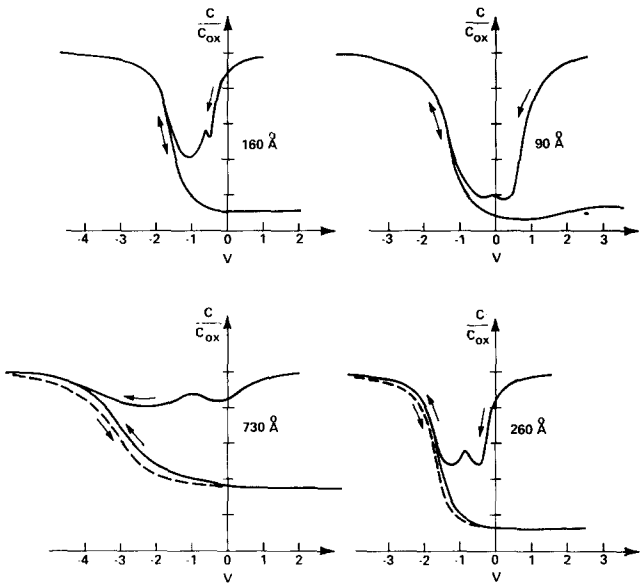

FIG. 1. High-frequency (1 MHz) and quasistatic C-V curves after radiation, for MOS samples with four different oxide thicknesses. The accumulated 25-keV electron dose is 0.95×10^{-5} C/cm^2. The vertical scale is normalized with respect to the oxide capacitance.

mated to be less than 200 °C, the wafer temperature during evaporation.

High-frequency (1 MHz) and quasistatic C-V data were taken to determine the initial surface-state density, which was found to be low, from 3×10^{10} to 6×10^{10}/cm^2, for all the samples.

The samples were then irradiated by a 25-keV electron beam scanning the entire surface of the wafer. No voltage was applied to the sample during the irradiation. The electron dose was calculated to be 0.95×10^{-5}C/cm^2. After the exposure, C-V measurements were taken again.

Figure 1 shows the C-V curves, both high-frequency and quasistatic, for MOS capacitors of four different thicknesses after irradiation. The data for the 2100-Å sample follow the same trend and are not shown here. As is easily seen, the quasistatic C-V curve deviates more and more from the high-frequency C-V curve as the oxide thickness increases. This indicates that the radiation causes more surface states in thicker oxide. The hysteresis in the high-frequency C-V curve is believed to be due to slow states induced by the radiation, and is also more pronounced for thicker oxide.

Figure 2 is a plot of the distribution of the surface states that the irradiation induced in the silicon band gap, with oxide thickness as a parameter. Three points can be noted. First, the over-all density increases monotonically with increasing oxide thickness. Second, for oxides more than 90 Å thick the shapes of the distribution curves are qualitatively the same, asymmetrical about the midgap and peaking about 0.2 eV from the midgap.[10] This result is similar to that reported earlier for MOS capacitors (500-Å oxide) with various silicon substrates.[5] Third, the thickness dependence is much greater in the peak region (about 0.2 eV) than in the tail region (about −0.4 eV).

To be certain that the results are not due to differences in the amount of electron energy that oxide layers of different thicknesses allow to reach the SiO_2-Si interface, an estimate of the electron energy E and the energy deposition rate E_d at the interface was calculated. A 4000-Å Al film was assumed for both samples. For the 90-Å sample, $E \simeq 23.5$ keV and $E_d \simeq 0.33$ eV/Å; for the 2100-Å sample, $E \simeq 23$ keV and $E_d \simeq 0.36$ eV/Å.[11] Thus, even for the thickest and thinnest samples, both E and E_d differ by no more than 10%, too little to account for the observed thickness dependence.

Nor does the hydrogen model[4,7] seem to explain the thickness dependence of the surface states induced by the radiation. Since all the oxides were grown in the same gas at the same temperature, one would not expect the hydrogen-related centers at the SiO_2-Si interface to increase systematically with increasing oxide thickness. Furthermore, as was pointed out earlier,[5] the hydrogen model calls for considerable electron trapping at the Si-SiO_2 interface,[7] but none was observed.

The results do seem to be consistent with the broken-bond model.[2,5,6] During the thermal oxidation, a number of strained bonds are formed in the SiO_2 film. The electron bombardment causes many of these strained bonds to break.[6] The resulting structural modification of the SiO_2 results in a shrinkage of the film.[2,12] Since the electron beam interacts with only a small spot of the film at any instant, only that spot tends to shrink, while the area surrounding it tends to remain unchanged. Within the spot, therefore, a stress is produced at both

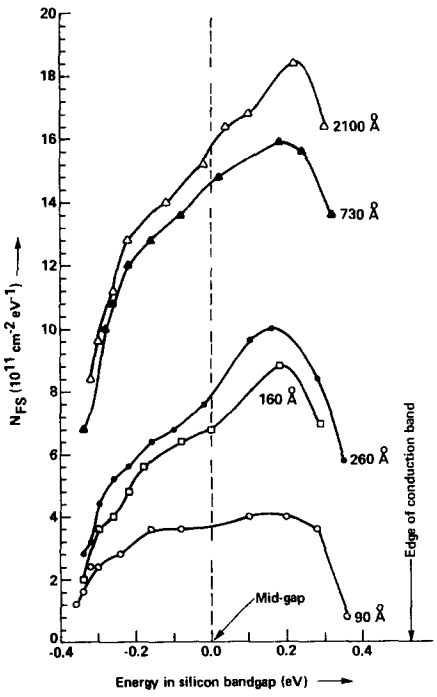

FIG. 2. Surface-state distribution in the silicon band gap after radiation, with oxide thickness as the parameter.

the metal-SiO_2 and the SiO_2-Si interfaces. If the stress is large enough, it causes many of the bonds at the SiO_2-Si interface to break. Both the stress and the broken bonds at the SiO_2-Si interface have been reported to cause surface states.[2,13–15]

A shift of the order of 1 Å of the SiO_2 film with respect to the silicon surface may be enough to create interfacial bond disorder, which will be detected as surface states. It has been reported that a SiO_2 film 1500 Å thick compacts to a thickness of 1300 Å for a low-energy electron (1—20 keV) exposure of 5×10^9 rad (Si).[2] The dosage used in the present investigation is equivalent to approximately 1×10^6 rad (Si), and therefore should be enough to produce a compaction of a few angstrom units by a linear extrapolation from the above data. Although this is only an order-of-magnitude estimate, it strongly suggests the likelihood of the broken-bond model for radiation-induced surface states.

If one assumes that the volume density of the initially strained bonds is about the same for a thin SiO_2 film as for a thick one, radiation will cause about the same percentage of shrinkage in both films. Therefore, the overall shrinkage of the thickness will be larger for a thicker film. Consequently, the induced stress and the number of broken bonds will also be larger for a thicker film. This is consistent with the present results.

Since slow states are believed to be electronic trap sites located in SiO_2 within tunneling distance from the interface,[16] they are probably also related to the broken bonds near the SiO_2-Si interface. Then the above reasoning can also be applied to explain our data on slow states: the thicker the film, the more slow states are generated by the radiation.

We did not attempt to explain the shape of the surface-state distribution observed after radiation (Fig. 2) or the energy at which the peak occurs, about 0.2 eV. Berman[17] reported a similar peak, which he suggested was a single-level acceptor-type surface state. The data reported here and in Ref. 5 suggest that the peak may be an intrinsic characteristic of the radiation-induced SiO_2-Si interface. More work needs to be done to understand this behavior.

The author would like to thank Dr. A. Berman for helpful discussions.

[1]J.R.Szedon and J.E. Sandor, Appl. Phys. Lett. **6**, 181 (1965).
[2]H.L. Hughes, IEEE Trans. Nucl. Sci. **NS-16**, 195 (1969).
[3]L.L. Sivo, H.L. Hughes, and E.E. King, IEEE Trans. Nucl. Sci. **NS-19**, 313 (1972).
[4]M. Pepper, Thin Solid Films **14**, S7 (1972).
[5]T.P. Ma, G.A. Scoggan, and R. Leone, Appl. Phys. Lett. **27**, 61 (1975).
[6]C.W.Gwyn, J. Appl. Phys. **40**, 4886 (1969).
[7]E.H. Nicollian, C.N. Berglund, P.F.Schmidt, and J.M. Andrews, J. Appl. Phys. **42**, 5654 (1971).
[8]T.P. Ma, G.A.Scoggan, D.J. DiMaria, and B. Yun (unpublished).
[9]There we found that electron radiation caused no increase in surface-state density for a 23-Å oxide MNOS memory dot, although the same electron radiation caused the surface-state density for a 325-Å oxide MNOS capacitor to increase by two orders of magnitude.
[10]The computer program used to calculate the distribution of surface states assumed a uniform concentration of boron on the sample. By taking into account the boron depletion resulting from thermal oxidation, a correction of -0.05 eV is estimated for this peak. A. Berman (private communication).
[11]Calculation based on the following paper: P.H. Hoff and T.E. Everhart, *Rec. 10th Symp. Electron, Ion, and Laser Beam Technology* (San Francisco Press, San Francisco, 1969), pp. 454—458.
[12]R.A. Sigsbee and R.H. Wilson, Appl. Phys. Lett. **23**, 541 (1973).
[13]C.H. Lane, IEEE Trans. Electron Devices **ED-15**, 998 (1968).
[14]B.E.Deal, J. Electrochem. Soc. **121**, 199C (1974).
[15]J.A. Appels, H. Kalter, and E. Kooi, Philips Tech. Rev. **31**, 225 (1970).
[16]F.P. Heiman and G. Warfield, IEEE Trans. Electron Devices **ED-12**, 167 (1965).
[17]A. Berman, Semiconductor Interface Specialist Conference, San Juan, 1974 (unpublished).

Photoemission study of the formation of Schottky barriers*

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For the first time, changes in electronic structure have been studied during Schottky barrier (Cs on GaAs or InP) formation. Strong changes occur near the valence band maximum; however, these do not overcome a dominant role of intrinsic surface states in Fermi-level pinning.

PACS numbers: 73.30., 73.20.H, 73.40.N, 79.60.G

Bardeen[1] explained semiconductor Schottky barriers in terms of Fermi-level pinning due to intrinsic surface states. This concept has been widely accepted and used with considerable success.[2] However, in the last decade, theoretical questions have been raised concerning the survival of intrinsic surface states when a metal overlayer is added to the surface[3] and new mechanisms have been advanced to explain the Fermi-level pinning

