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J. D. McBrayer, R. M. Swanson and T. W. Sigmon

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therefore, only apparently discharge cleaned, even after prolonged Ar^+ ion sputtering [see (i), above]. When the applied voltage is increased, some of the remaining fluorine atoms are again within the range of the more energetic ions, but the many reactive defects created in their vicinity bind these fluorines, and prevent their release at a level above the detection limit. Finally, when new NF_3 is introduced (second NF_3 pulse shown in Fig. 4) the partially fluorinated defects cause the dissociation of some of the NF_3 and the product release seen as the S.T.

Very careful spectroscopic work would be required in conjunction with the pulse injection experiments to characterize the defects further, involving techniques such as RBS, ESR, and RHEED (3), and to test the above ideas. Specifically, one might wish to confirm that "clean" defects do not cause NF_3 to dissociate [see (i), above], but partially fluorinated ones do.

The versatility of the procedures used here was exploited in several additional ways which should be mentioned, briefly:

First, the NF_2^+ and NF^+ mass signal transients are known from earlier work to be representative of the unfragmented NF_3 present in the gas phase (7). If one superposes plasma and NF_3 pulses, but extinguishes the plasma during the gas pulse, one finds the above signals to increase above their plasma-on level, and one can thus estimate the half-time for recombination of the fragments present. This is about 0.6s for the present cell and a flow rate of 0.07 sccm.

Second, the same experiment leads to an abrupt end of the product release, within experimental errors. So the effect of unfragmented NF_3 is relatively small, even right after the surface has been ion bombardment damaged. This is consistent with the observed S.T.'s discussed above since the latter transients account for only a small fraction, perhaps 0.5-3%, of the total product released during the I.T.'s, and these in turn are much smaller than the product transients obtained during normal etching, as discussed earlier (7).

Conclusions

Applying short pulses of a dc discharge to a Si sample previously etched under NF_3 leads to the stepwise cleaning of this surface, but a small portion of the fluorine

stored in near-surface regions probably remains, even after this treatment.

Injecting very short pulses of NF_3 after the plasma pulses leads to the release of additional small amounts of residual fluorine, as SiF_4 , a process presumably depending upon the creation of ion bombardment induced defects in surface near layers, and the presence of minute amounts of residual fluorine.

There are indications that some of the fluorine stored in near-surface regions during etching diffuses into deeper layers, beyond the ion-damaged regions.

The half-times for some of the above processes have been estimated, and the versatility of the pulse injection procedure has been explored in several ways.

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Diffusion of Metals in Silicon Dioxide

J. D. McBrayer, R. M. Swanson,* and T. W. Sigmon*

Stanford Electronics Laboratories, Stanford, California 94305

ABSTRACT

The diffusion coefficient and solubilities of several metals (Ag, Cu, Au, Pd, and Ti) have been investigated by bias temperature stress (BTS) of metal/ SiO_2 /Si (MOS) structures using the candidate metal as the electrode. Temperatures ranged from 250° to 600°C, and the electric fields ranged from $+10^6$ to -10^6 V/cm in ambients of vacuum (10^{-6} torr), nitrogen (N_2), and forming gas (N_2H_2). In dry N_2 (<3 ppm H_2O), the activation energy for silver diffusion is found to be 1.24 eV in the temperature range of 275°-365°C. The diffusion coefficient for silver at 300°C in silicon dioxide is 4.5×10^{-13} cm^2/s . Copper diffusion has an activation energy of 1.82 eV in the temperature range of 350°-450°C in a forming gas environment (<3 ppm H_2O) and a diffusion coefficient in SiO_2 at 450°C of 1.2×10^{-11} cm^2/s . A thermodynamic model to predict the activation energy of the solid solubility of these metals in SiO_2 and an interstitial diffusion model, that includes both strain and electrostatic energies, which predicts the diffusion activation energy, have been developed. Diffusion coefficients are estimated from a closed form solution of the diffusion equation and the observed behavior of the metal in SiO_2 .

During the last several years, an effort has been undertaken by many development groups to find a replacement/alternative to the Al/AlCuSi doped polysilicon metallization systems for use in Si integrated circuit fabrication. The use of other metals and metal silicides for contacts, interconnects, and gates has been thoroughly investigated (1, 2). Although several of these metallization systems show promise (3), only a few (4) are presently

used in producing integrated circuits. Furthermore, there is little information on the long term stability of devices fabricated with these metallization systems.

Therefore, it is the purpose of this paper to address one important aspect of this reliability problem—that is, solubility and diffusion of a candidate metal through device quality SiO_2 during low temperature bias temperature stress (BTS). The possible effects on metal-oxide semiconductor-transistor (MOST) performance is discussed.

*Electrochemical Society Active Member.

Experimental Processing

Circular metal-oxide-silicon (MOS) structures of various diameters (0.5-2.5 mm) were fabricated by evaporating the metal under investigation through a molybdenum dot mask onto SiO_2 films. The oxide films are device quality SiO_2 layers grown using both wet and dry oxidation conditions on n-type $3 \rightarrow 6 \Omega\text{-cm}$ <100> Czochralski (CZ) silicon. These oxides were 5000Å thick or thicker. (Investigation of oxides thinner than 1000Å did not yield reproducible results and are not discussed here.) Following oxidation, but prior to candidate metal evaporation, the back surface of the wafers are stripped of their SiO_2 film and given a heavy n^+ diffusion for contacts. Approximately $1.0 \mu\text{m}$ of Al is then evaporated onto these surfaces and sintered at 450°C for 20 min in N_2 . This step provides a back surface electrical contact for the structures. The wafers are then prepared for BTS measurements by evaporation of either Cu, Ag, Au, Pd, or Ti onto the oxide-covered surface.

The BTS measurements are carried out in ambients of N_2H_2 , N_2 , and vacuum ($\sim 10^{-6}$ torr). Temperatures used ranged from 250° to 600°C and electric fields between $\pm 10^6$ V/cm. For these experiments, a positive electric field is defined as when a positive voltage is applied to the metal under investigation with respect to the back Al contact.

Experimental Measurements

We used capacitance-voltage measurements (C-V) at 1 MHz (5) and Rutherford backscattering spectrometry (RBS) (6) with 2.2 MeV $^4\text{He}^+$ ions as the primary techniques for measurement of the metal diffusion in the oxides. The C-V measurement provides a sensitive test for metal contamination of the SiO_2/Si interface following BTS with a detection sensitivity approaching 10^9 at./ cm^2 (assuming singly ionized metal atoms).

For the actual identification and measurement of the number of metal atoms diffusing through the oxide, RBS measurements are used. This measurement technique allows tracking the diffusion of the various metals for areal densities exceeding $\sim 10^{14}$ at./ cm^2 for the different BTS treatments. Also, information regarding pile-up of the metal at the SiO_2/Si interface is obtained.

Experimental Results

During the course of this work, the structures previously described were fabricated using the metals mentioned earlier for the top electrode. BTS measurements were performed on these structures at temperatures from 250° to 600°C and electric fields from -10^6 to $+10^6$ V/cm. Ambients were dry N_2 (<3 ppm H_2O), forming gas (N_2H_2), and vacuum (10^{-6} torr). Electrical measurements (C-V) were performed to access the effect of the BTS on the electrical properties of the interface. RBS measurements were performed to measure the amount of metal that diffused in/through the oxide.

The C-V measurements revealed no changes for the negative and zero biased experiments. For positive biased experiments, the sensitive C-V measurements were completely overwhelmed. That is, once the activation of the field added diffusion occurred, the metal atoms moved very quickly and in such large quantities that any quantitative information was lost. From these C-V measurements, we can conclude whether or not a metal diffuses through the SiO_2 and that, in all cases, the metals that do diffuse do so as a positively charged species.

In Fig. 1, we show an RBS spectra taken on a $\text{Cu}/\text{SiO}_2/\text{Si}$ structure following BTS for one (— — —) and two (· · · · ·) hours at 450°C and $+5 \times 10^4$ V/cm. The Cu electrode has been removed following the BTS treatment to enhance the measurement sensitivity. To aid interpretation of the data, signals corresponding to $^4\text{He}^+$ backscattered from atoms at the surface and interface are marked. From these data, one can see that the Cu has diffused into the region near the Si/SiO_2 interface.

Verification that this is Cu at the SiO_2/Si interface is obtained by tilting the sample a known angle with respect

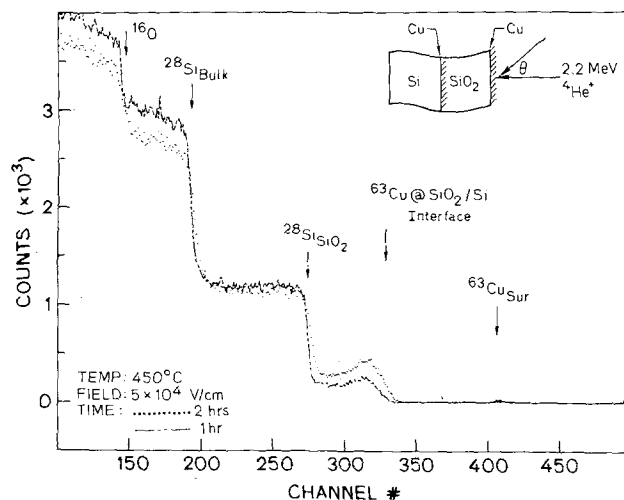


Fig. 1. Backscattering spectra for Cu diffused SiO_2/Si layer. BTS conditions were 450°C with an electric field of $+5 \times 10^4$ V/cm for (— — —) 1h and (· · · · ·) 2h. Analyzing beam was 2.2 MeV $^4\text{He}^+$ a detector angle $\theta = 10^\circ$.

to the incoming beam. Also, since the width of the Cu peak is greater than the system energy resolution (~ 7 channels), this indicates that the Cu is diffusing into the silicon substrate. This is in contrast to our earlier findings for silver (7).

The flux of Cu and Ag through the oxide at any given temperature can be found from the slope of the concentration- cm^{-2} vs. time data. In Fig. 2, we show an Arrhenius plot of Cu and Ag concentration- cm^{-2} vs. $(\text{kT})^{-1}$. The activation energies for the diffusion process are found from these data and are 1.24 eV for Ag (dry N_2) and 1.82 eV for Cu (N_2H_2). The apparent saturation of Cu above 450°C is

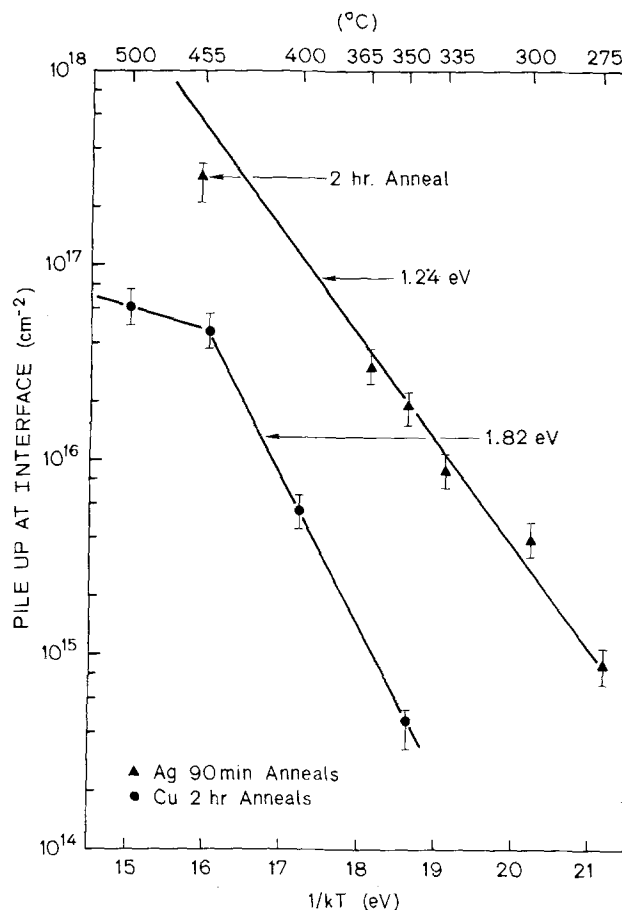


Fig. 2. Arrhenius plot of the amount of Ag (▲) and Cu (●) found at the SiO_2/Si interface following BTS. The calculated activation energies are $E_A^{\text{Ag}} = 1.24$ eV and $E_A^{\text{Cu}} = 1.82$ eV.

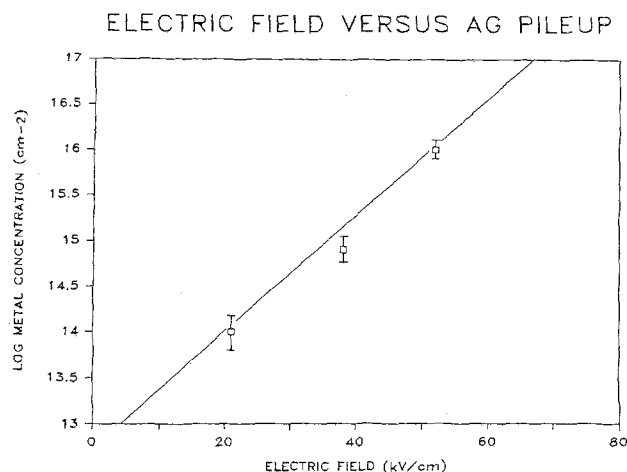


Fig. 3. Electric field vs. silver pile-up at the SiO_2/Si interface

an artifact of the experiment caused by oxidation of the Cu electrode with a resulting loss of electrical contact.

Figure 3 plots silver pile-up vs. electric field. Each experiment was done at 335°C for $1\frac{1}{2}\text{h}$. The logarithmic, linear plot indicates that the electric field aided diffusion process is exponentially dependent on electric field.

Analysis and Discussion

Our experimental results suggest that Ag and Cu diffuse as positive ions in SiO_2 since there is no detectable diffusion when the field is reversed. For the case, where the drift term dominates the diffusion equation, the flux (J) of positive ions can be written as

$$J = -\frac{q}{kT} DC_{ss}\epsilon \quad [1]$$

Here, D is the diffusivity, C_{ss} the solid solubility of the diffusing species in the medium, ϵ the electric field, q the electronic charge, k Boltzmann's constant, and T the temperature. The concentration gradient portion of the flux can be ignored compared to the electric field term since no detectable diffusion is observed for the zero and negatively biased cases investigated.

The measured flux J of atoms through the SiO_2 depends on the diffusivity D and the solid solubility C_{ss} of the metal in the SiO_2 . Both of these terms have their own activation energies.

For the case of metals which diffuse as interstitials in SiO_2 (8, 9), the diffusivity can be expressed as

$$D = D_0 e^{-E_{\text{diffusion}}/kT} \quad [2]$$

where D_0 is the diffusion constant and $E_{\text{diffusion}}$ is the activation energy for diffusion.

Following the approach of Zener (8), we may estimate a lower limit for D_0 to be $D_0 \approx b^2\nu \approx 0.025 \text{ cm}^2 \text{ s}^{-1}$ based on a lattice spacing $b \approx 5\text{\AA}$ and a lattice vibration frequency $\nu = 10^{13} \text{ Hz}$ for SiO_2 (10, 11). This value for D_0 will be used throughout the following discussion.

We use the classical approach described by Anderson and Stuart (12) to calculate the activation energy of metal diffusion in SiO_2 . In this model, the activation energy is assumed to be the sum of two terms: (i) the strain interaction term between the diffusing atom and the SiO_2 lattice and (ii) the electrostatic interaction term between a charged diffusing atom and the SiO_2 lattice. Using available material parameters, we show results of this calculation for singly ionized atom diffusion in SiO_2 in Fig. 4.

We derive the solid solubility of a metal in silicon dioxide from solutions of the thermodynamic equations for each possible diffusing species. The important assumption that makes this derivation possible is that the ideal gas law holds for metals in the loose structure of silicon dioxide. This allows us to calculate the concentration of a

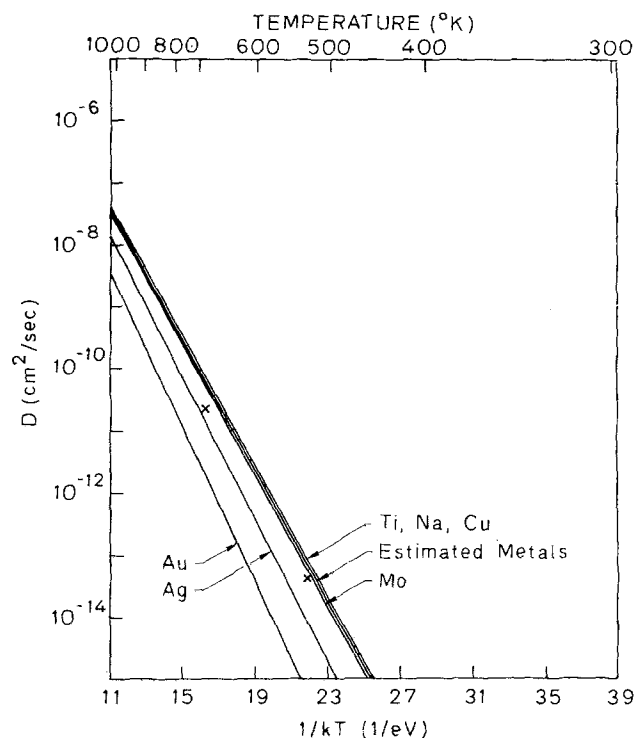


Fig. 4. Theoretical calculation of the diffusivity of singly ionized atoms in SiO_2 vs. reciprocal temperature. The cross at 700 K is the experimental result obtained for Cu, while the one at 573 K is for Ag.

metal in silicon dioxide as a function of the concentration of the metal vapor.

The solution of a set of thermodynamic equations in equilibrium is independent of the path taken. As an example, one solution path for the singly ionized case follows: the metal is first vaporized by applying the heat of sublimation, ΔH_{sub} . The metal vapor is ionized by providing the heat of ionization, ΔE_{ion} . To place both the ionized metal and the free electron into the silicon dioxide, the needed heat of formation is given by the sum of three terms: (i) the heat of formation of the image charge, (ii) the binding energy for the positive ion and the electron affinity for the electron, and (iii) any other heat of formation such as that supplied by a deep level acceptor in the SiO_2 .

A graphic illustration of the above solution path is shown in Fig. 5 and 6. Figure 5 shows how the electrons and ions get into the SiO_2 , described previously. Figure 6 shows that an electron gives up at least an energy of χ upon entering the SiO_2 . In addition, if there are any deep acceptor levels in the SiO_2 , additional energy can be released. That is, if there are any deep level acceptors available to capture the electron, then the ion and electron will not recombine and the ionized atom will be available for electric field-aided diffusion. More is said about the role of deep level acceptors later.

Combining these processes for singly ionized diffusors yields the following thermodynamic equation

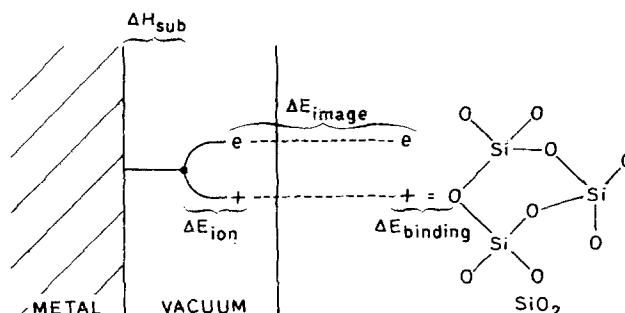


Fig. 5. Schematic of the thermodynamic solution path for singly ionized diffusion in SiO_2 from a surface metal source.

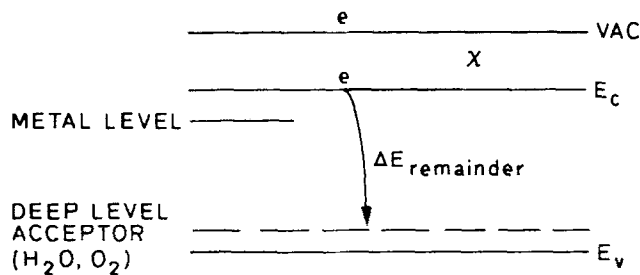


Fig. 6. Band diagram of SiO_2 illustrating the effect of a deep level acceptor.

$$M_{\text{sol}} \rightleftharpoons M_{\text{ox}}^+ + e_{\text{ox}}^-; \Delta H_{\text{sub}} + \Delta E_{\text{ion}} - \Delta E_{\text{binding}} - \Delta E_{\text{remainder}} \quad [3]$$

where M_{sol} is the metal as a solid, M_{ox}^+ is the ionized metal in the silicon dioxide, e_{ox}^- is the free electron in the silicon dioxide, ΔH_{sub} is the heat of sublimation of the metal into its vapor, ΔE_{ion} is the ionization potential for the metal, $\Delta E_{\text{binding}}$ is the coulombic binding energy of the metal to the O^- in SiO_2 , and $\Delta E_{\text{remainder}}$ is twice the image charge heat of formation plus the electron affinity plus any other heat of formation.

Applying the law of mass action between the ionized species and the neutral species results in

$$\frac{[M_{\text{ox}}^+][e^-]}{[M_{\text{gas}}]} = e^{-[-\chi_{\text{MON}} + \chi_{\text{eox}} - \chi_{\text{Mgas}}]} \quad [4]$$

where $[e^-]$ is the concentration of free electrons at the conduction band minimum in the oxide, $[M_{\text{gas}}]$ is the concentration of the metal in the gas phase and

$$\begin{aligned} \chi_{\text{Mox}^+} &= \ln \left(\frac{2\pi h^2}{m_{\text{M}} kT} \right) + \frac{E_{\text{Mox}^+}}{kT} \\ \chi_{\text{eox}^-} &= \ln \left(\frac{2\pi h^2}{m_{\text{e}} kT} \right) + \frac{E_{\text{eox}^-}}{kT} \\ \chi_{\text{Mgas}} &= \ln \left(\frac{2\pi h^2}{m_{\text{M}} kT} \right) + \frac{E_{\text{Mgas}^+}}{kT} \end{aligned} \quad [5]$$

Substituting

$$\frac{[M_{\text{ox}}^+][e^-]}{[M_{\text{gas}}]} = \left(\frac{m_{\text{e}} kT}{2\pi h^2} \right)^{3/2} e^{\frac{-[E_{\text{Mox}^+} + E_{\text{eox}^-} - E_{\text{Mgas}}]}{kT}} \quad [6]$$

The energy term in the argument of the exponential can be equated with the energy term in Eq. [3] without the heat of sublimation as follows

$$E_{\text{Mox}^+} + E_{\text{eox}^-} - E_{\text{Mgas}} = E_{\text{ion}} - E_{\text{binding}} - E_{\text{remainder}} = E_{\text{int}} \quad [7]$$

where, as described above and illustrated in Fig. 4 and 5

$$\begin{aligned} E_{\text{ion}} &= E_{\text{Mgas}^+} + E_{\text{eox}^-} - E_{\text{Mgas}} \\ E_{\text{Mgas}^+} - E_{\text{Mox}} &= E_{\text{binding}} + E_{\text{image}} \\ E_{\text{eox}^-} - E_{\text{eox}} &= \chi + E_{\text{image}} + E_{\text{unknown}} \\ E_{\text{remainder}} &= \chi + 2E_{\text{image}} + E_{\text{unknown}} \end{aligned} \quad [8]$$

Using charge conservation, $[e^-] = [M_{\text{ox}}^-]$, results in

$$[M_{\text{ox}}^+] = [M_{\text{gas}}]^{1/2} \left(\frac{m_{\text{e}} kT}{2\pi h^2} \right)^{3/4} e^{\frac{-E_{\text{int}}}{2kT}} \quad [9]$$

If we assume that there is no interaction or binding of the neutral metal species with the silicon dioxide and that the metal atomic radius ($<2\text{\AA}$) is somewhat less than the interstitial dimensions of the silicon dioxide ($>5\text{\AA}$), then in thermal equilibrium the concentration of neutral metal in the silicon dioxide, $[M_{\text{ox}}]$, will be approximately equal to that of the metal vapor in an otherwise empty region, $[M_{\text{gas}}]$. In other words, as far as the neutral species is concerned, the presence of the silicon dioxide has no effect. This approximation is obviously not valid for network

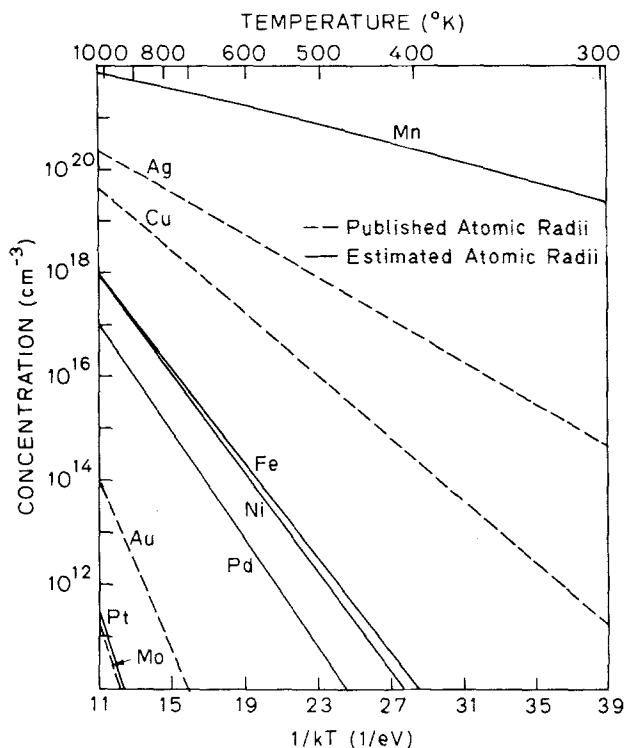


Fig. 7. Calculated solid solubility for singly ionized atoms in SiO_2 using the approach described.

formers, such as B, P, or metals which react strongly with silicon dioxide, such as Al or Ti.

Using the ideal gas law to relate the vapor concentration of a metal to its vapor pressure and using the standard form for expressing vapor pressure (13), we obtain

$$\begin{aligned} [M_{\text{ox}}^+] &= 1.527 \times \\ &\times \frac{10^{(R/2+17)} e^{\frac{+(E_{\text{int}} + kA \ln 10 - (kT^2 D \times 10^{-3} \ln 10) - kT/2 (2C+1) \ln T)}{2kT}}}{1} \end{aligned} \quad [10]$$

In the above equation, A, B, C, and D are constants that describe the vapor pressures for each metal, N-Avogadro's number, and the gas constant R. Combining the above equations with published vapor pressure and ionization potential data, calculated binding energies and experimentally determined remainder energies, the solid solubility for singly ionized atoms in SiO_2 are calculated and plotted in Fig. 7.

In general, the solid solubility takes on the form

$$C_{\text{ss}} = C_0 e^{-E_{\text{ss}}/kT} \quad [11]$$

for all diffusing species. The singly ionized case has been presented since the higher ionized states yield a much lower solid solubility for most metals. For further information, see Ref. (14). A negative value for E_{ss} implies that the atom in question would rather be in the oxide than out.

The diffusion coefficients for silver and copper are found in Eq. [1]. The flux term is determined experimentally from measurement of the number of atoms piled up at the interface for various anneal times. We estimate an upper limit for the solubility of Ag from RBS measurements to be $3 \times 10^{18} \text{ cm}^{-3}$. Since we were unable to detect Cu in the oxide for short diffusion times, we must assume that C_{ss} for Cu in SiO_2 is below the detection sensitivity of our measurement. We then use the Ag results to calculate $\Delta E_{\text{remainder}} = 8.87 \text{ eV}$. Using this value in Eq. [7] allows calculation of E_{int} which, when used in Eq. [10], allows calculation of E_{ss} for Cu and thus C_{ss} for Cu in SiO_2 . The results are tabulated in Table I for Cu and Ag.

We may write the flux of atoms through the SiO_2 as

Table I. Summary of copper and silver. Predicted and observed diffusivity and activation energies

	Silver		Copper	
	Vacuum 528°C	Atmosphere N ₂ 300°C	Vacuum 528°C	Atmosphere H ₂ N ₂ 450°C
Solid solubility (cm ⁻³)				
Observed	Not detectable	3 × 10 ¹⁸	Not detectable	Not detectable
Predicted	10 ⁹	—	10 ⁷	10 ¹⁸
Diffusivity (cm ² /s)				
Observed	Not detectable	4.5 × 10 ⁻¹³	Not detectable	1.2 × 10 ⁻¹¹
Predicted	10 ⁷	9.2 × 10 ⁻¹⁴	5 × 10 ⁻⁴	1.2 × 10 ⁻¹⁰
Activation energy (eV)				
Observed	Not detectable	1.24	Not detectable	1.82
Predicted				
Diffusion	1.30	1.30	1.20	1.20
Solid solubility	6.10	0.49	6.72	0.64

$$J = -\frac{q}{kT} \epsilon D_0 C_0 e^{-(E_{\text{diffusion}} + E_{\text{ss}})/kT} \quad [12]$$

Using the calculated values for $E_{\text{diffusion}}$ and the values for E_{ss} determined experimentally and as described above, we arrive at a total activation energy of

$$E_A^{\text{Ag}} = E_{\text{diff}}^{\text{Ag}} + E_{\text{ss}}^{\text{Ag}} = 1.3 + 0.5 = 1.8 \text{ eV}$$

and, for Cu

$$E_A^{\text{Cu}} = E_{\text{diff}}^{\text{Cu}} + E_{\text{ss}}^{\text{Cu}} = 1.2 + 0.64 = 1.84 \text{ eV}$$

These values are to be compared with those determined experimentally of $E_A^{\text{Ag}} = 1.24 \text{ eV}$ and $E_A^{\text{Cu}} = 1.82 \text{ eV}$, quite reasonable agreement considering the complexity of the problem.

The diffusion of Au and Pd were undetectable by both RBS and C-V measurements for temperatures up to 600°C and fields as high as $\pm 10^6 \text{ V/cm}$. These results are expected in light of the prediction of the model for low solid solubility for both of these elements. Titanium was found to react with the silicon dioxide to form a titanium oxide and is thus not expected to diffuse. This result has recently been predicted using a ternary phase diagram analysis (15).

A unique aspect of this work was the discovery that the diffusion of both Cu and Ag could be suppressed by providing a vacuum ($\sim 10^{-6}$ torr) ambient. As a check, experiments were also performed with the vacuum chamber back-filled with 50 torr of N₂. Following a 3h BTS at 355°C and $+10^5 \text{ V/cm}$, silver was again observed at the SiO₂/Si interface. However, this time, the amount of Ag was about two orders of magnitude less than that observed under an atmospheric N₂ ambient.

Residual gas analysis of the N₂ found traces (<3 ppm) of H₂O, O₂, and numerous organic compounds. Both H₂O and O₂ are reported (16-18) to cause deep level traps in SiO₂. We speculate that the deep level acceptors in the SiO₂ forbidden gap lowers the Fermi level which results in more efficient ionization of the neutral metal atoms in the oxide. Without these levels, the metal ions and the free electrons eventually recombine and lower the total number participating in the field-aided diffusion process.

The role of these residual gases also explains why there is no observed difference between wet and dry oxides. That is, since both H₂O and O₂ diffuse through SiO₂ so quickly, even at room temperature (19), any exposure to room ambient will leave plenty of deep level acceptors around to aid the diffusion process, thus making the behavior of the two types of oxides very similar.

Summary

We have investigated the low temperature electric field aided diffusion of several metals in SiO₂. By assuming that the electric field term dominates the diffusion process, the metal atoms diffuse interstitially, the ideal gas

law holds for metals in silicon dioxide ($[M_{\text{ox}}] = f[M_{\text{ss}}]$), and that the remaining energy is approximately equal for all metals of like ionization state, a model which considers both the solid solubility and diffusion of these metals in SiO₂ has been presented. By using this model, we are able to predict the observed diffusion coefficients for Ag and Cu in silicon dioxide. We also observed the effect of deep level electron traps on the ionization of these metals in the SiO₂.

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