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INVESTIGATION OF METALLIC IMPURITIES INTRODUCED INTO SIO_2

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SUMMARY

This report contains the theoretical development of a model that describes the diffusion of interstitial diffusors in SiO_2. Experimental data supporting this model and the implications and conclusions predicted by this model are presented.

In summary this model concludes that Pd, Au, Mo, Ta, W, Pt, Ti, and Al are potential candidates for use in VLSI gate metalization schemes, where as Ag, Cu, Na, Ni, Mn, Fe, Mg and Ga are unsuitable.

PUBLICATIONS

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J. D. McBrayer, R. M. Swanson, T. W. Sigmon and J. Bravman, "Observation of Rapid Field Aided Diffusion of Silver in Metal-Oxide-Semiconductor Structures.", Stanford University., Stanford, California 94305. Applied Physics Letters. Oct. 1983

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Letter on file

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Chapter I
MODELING

A complete derivation of the diffusion equation is found in the Appendix along with analytical solutions for some interesting boundary conditions. In this chapter a new diffusion and solid solubility model is presented that allows calculation of the diffusion and solid solubility activation energy. Comparison of this model with experimental data is done in chapter II.

A. Interstitial Diffusion

The diffusion of metals in silicon dioxide is assumed to be interstitial in nature [1.1, 1.2] . The diffusivity or diffusion coefficient for this type of diffusion is given by the following expression:

$$D = D_o e^{\frac{-E_a}{kT}} \tag{1.1}$$

where E_a is the activation energy for diffusion, k is the Boltzmann constant, T is the temperature and D_o is the diffusion constant.

To evaluate the diffusion coefficient at a given temperature the values of D_o and E_a must be known. The following two sections will allow us to estimate their values in terms of fundamental quantities.

1. Diffusion Constant, D_o

Using the Zener theory [1.1] to predict D_o allows us to write

$$D_o = \rho b^2 \nu \eta f e^{\frac{S_a}{k}} \tag{1.2}$$

where ρ is the probability of an interstitial jump, b is the jump distance, η is the number of equivalent jump paths, ν is the lattice vibration frequency, f is the correlation factor, k is the Boltzmann constant and S_a is the entropy.

From this equation we see that D_o depends upon the crystal structure of the lattice through which the diffusor is traveling. In all cases S_a will be a positive number [1.1] so that D_o will have a lower limit of

$$D_o \succeq \rho b^2 \nu \eta f \tag{1.3}$$

To first order

$$\rho \eta f \approx 1 \tag{1.4}$$

So that

$$D_o \approx b^2 \nu \approx .025 cm^2/sec \tag{1.5}$$

is the lower limit for D_o. This calculation used a lattice spacing for SiO_2 of 5 Å and a lattice vibration frequency of $10^{13} hz/sec$ [1.3, 1.4] We will use this number as an estimate of D_o in our future predictions of D.

2. Activation Energy of Diffusion, E_a

To calculate the activation energy of metal diffusion in silicon dioxide we use a classical approach introduced by Anderson and Stuart in 1954 [1.5]. In this model they assume that the activation energy is the sum of two terms; the first is the strain energy between the lattice structure and the diffusing atom, and the second is the electrostatic energy between a charged diffusing species and the silicon dioxide lattice. We consider each in the following sections.

a. Strain Energy

We first assume that the strain energy generated in a silicon dioxide network due to the enlargement of a spherical doorway, of radius r_d, to accommodate an ion of radius r is approximately the elastic energy required to dilate a spherical cavity from radius r_d to r. This strain energy (E_s) is given by

$$E_s = 4\pi G r_d (r - r_d)^2 \tag{1.6}$$

where G is the shear modulus for silicon dioxide, $G = 3.12 \times 10^{11} dynes/cm^2$ [1.4], r_d is the radius of the window through which the diffusing atom must pass, $r_d = 0.6$ Å [1.5], and r is the radius of the diffusing atom. The above expression is reduced by a factor of two from the exact mathematical solution to account for the very loose structure of silicon dioxide.

b. Electrostatic Energy, E_b

We will approximate the electrostatic energy change by

$$E_b = \frac{\beta z z_o e^2}{\gamma(r + r_o)} \tag{1.7}$$

after Anderson and Struart [1.5]. where β is the finite displacement factor in angstroms, given by

$$\beta = \frac{2.1 - r}{3.5} \tag{1.8}$$

and r is the radius of the diffusing species. The geometric factors are determined by assuming an interstitial diffusion jump distance of 7 Å and an atomic radius for oxygen (r_o) of 1.4 Å. The charge states of the diffusing species and the oxygen in the silicon dioxide lattice are z and z_o respectively, for oxygen z_o is 2. γ is approximately the dielectric constant of silicon dioxide, $\gamma = 3.9$.

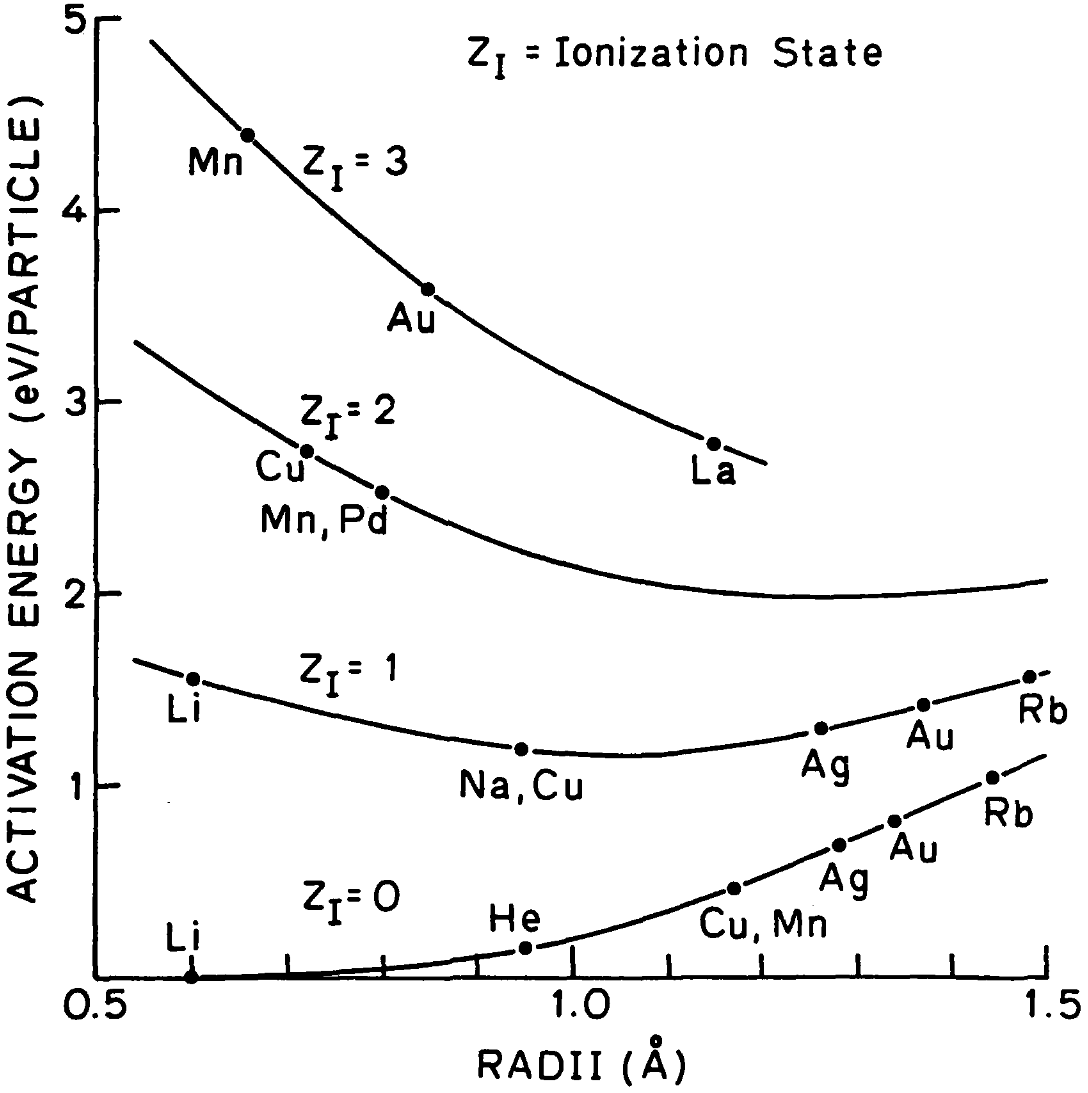

Figure 1.1. Interstitial Diffusion Activation Energy. Interstitial diffusion activation energy calculated by the sum of the strain energy and the change in the electrostatic energy.

c. Activation Energy, E_a

Combining the strain energy, E_s, and the electrostatic interaction energy, E_b, yields the total interstitial diffusion activation energy. The material parameter table found in Appendix A contains the known atomic radii for various neutral and ionized metal atoms. Using these numbers and those presented allows the generation of Fig. [1.1]. Figure [1.1] allows us to predict the activation energy for interstitial diffusion in SiO_2 for atoms with known atomic radii.

3. Diffusion Constant for Interstitial Diffusion

Having values for D_o and E_a allows prediction, via Eqn. (1.1) of the interstitial diffusion coefficient for elements that we believe diffuse interstitially. Figures [1.2 – 1.4] present the calculated Diffusivity for various metals and their ions in SiO_2. The data used in the calculation of the figures are found in Appendix A. Values appearing in the tables in brackets represent estimated values, for elements which no published data could be found.

In the next section we derive an equation for determining the solid solubility for these metals in silicon dioxide.

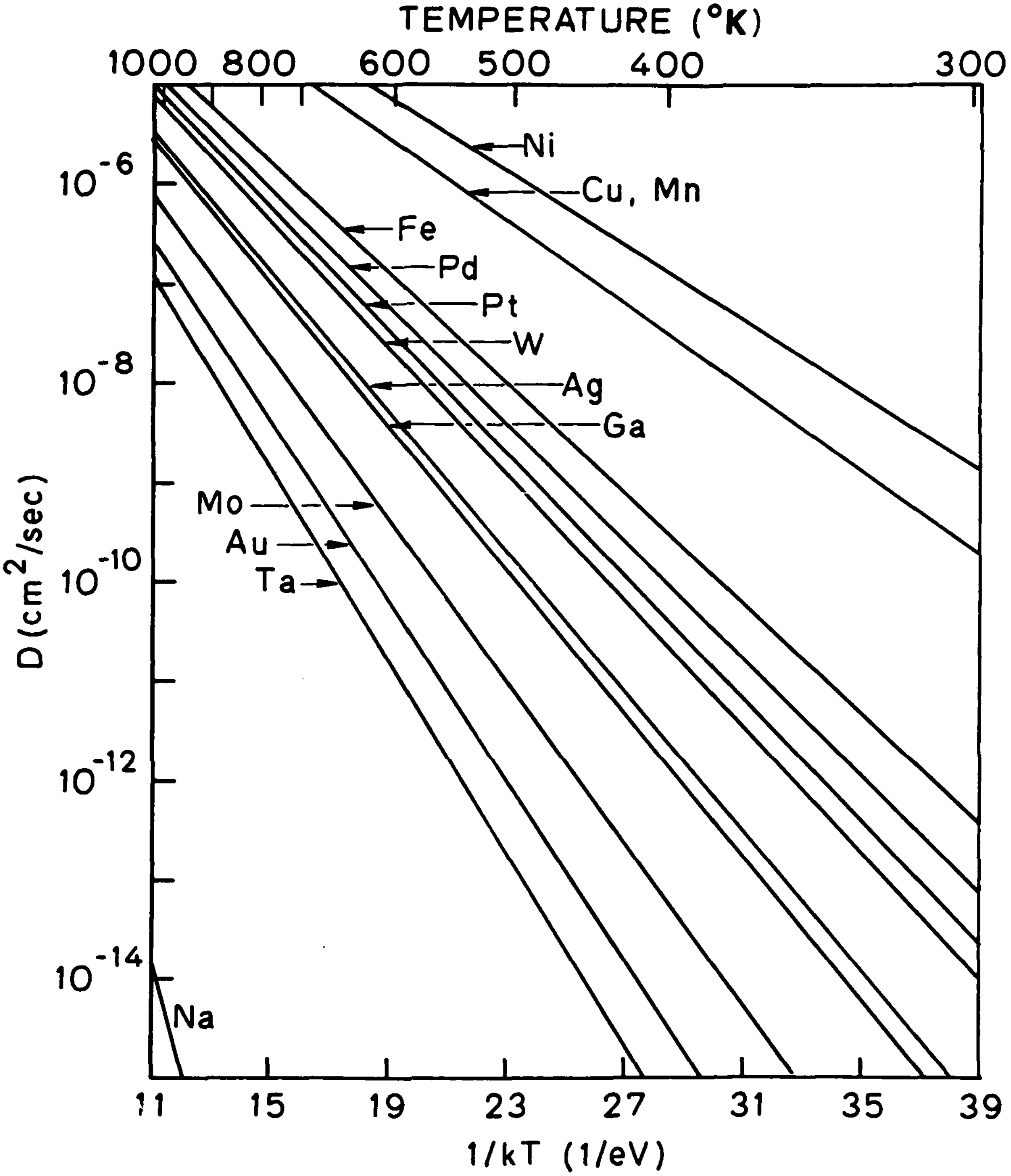

Figure 1.2. Predicted Neutral Diffusion Coefficients. Calculated Diffusivity for the indicated metals in silicon dioxide as a function of temperature.

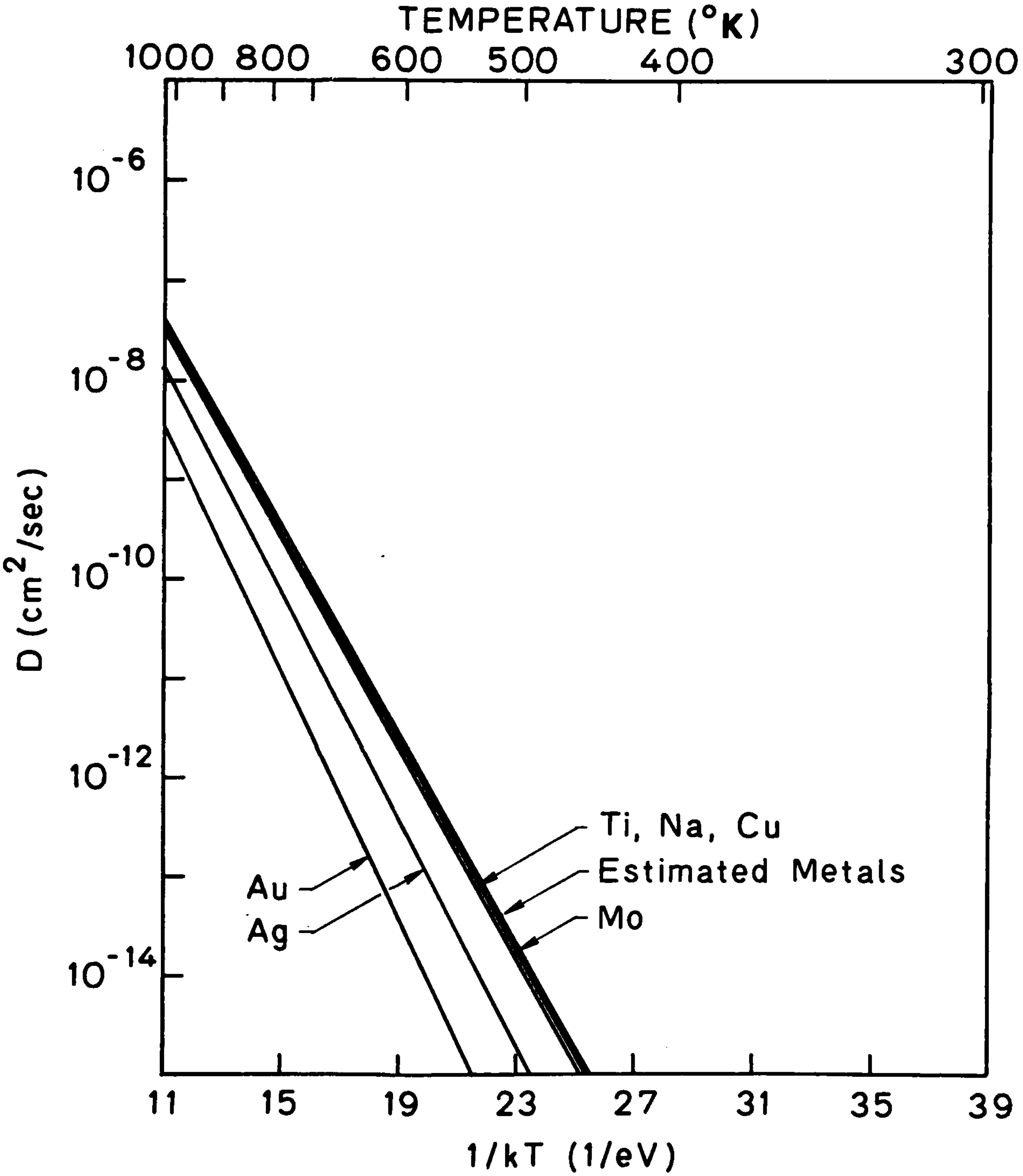

Figure 1.3. Singly Ionized Diffusivity. Calculated Diffusivity for singly ionized atoms.

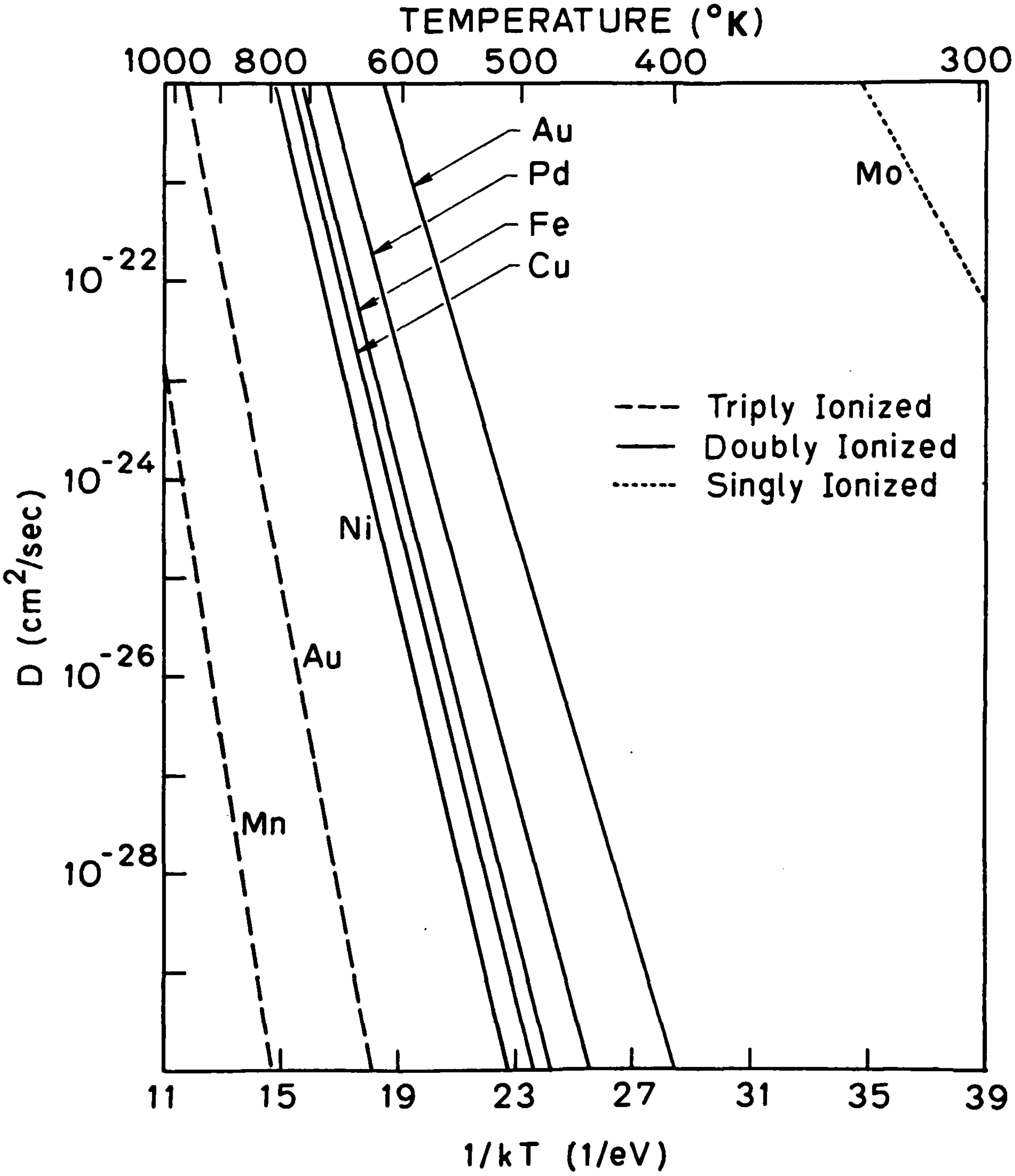

Figure 1.4. Predicted Ionized Diffusivity. Calculated Diffusivity for doubly and triply ionized atoms.

B. Solid Solubility

The solid solubility of metals in silicon dioxide is derived from solutions of the thermodynamic equations for each possible diffusing species. See Appendix B for derivation of the law of mass action and chemical potential.

The important assumption that makes this derivation justifiable is that the ideal gas law holds for the loose structure of silicon dioxide. This allows us to calculate the concentration of metal in silicon dioxide as a function of the concentration of metal vapor. In the following sections we will derive the concentration of neutral, singly, doubly, and triply ionized metal atoms in silicon dioxide or any other loosely bound lattice utilizing the above assumption.

1. Neutral Diffusors

Using the law of mass action we write the concentration of neutral metal atoms $[M_{ox}]$ in silicon dioxide as

$$[M_{ox}] = [M_{gas}]e^{\frac{-E_{int}}{kT}} \tag{1.9}$$

where E_{int} is the total internal energy and is the sum of the internal energy of the silicon dioxide, $E_{M_{ox}}$, plus that of the gas, $E_{M_{gas}}$. The internal energy, in this case, is equal to zero since we are assuming that the ideal gas law holds, i.e. $E_{M_{ox}} = E_{M_{gas}}$. k is the Boltzmann constant and T is the temperature. The concentration of metal that sublimes from the solid in accordance with the ideal gas law, $[M_{gas}]$, can be expressed as

$$[M_{gas}] = \left(\frac{N10^{B}T^{C-1}}{R}\right)e^{\frac{-A}{T}ln10+(DT\times 10^{-3}ln10)} \quad (1.10).$$

In the above equation A, B, C, and D are constants that describe the vapor pressures for each metal. [1.6] See material parameter table in Appendix A. N is Avogadro's number, $6.023 \times 10^{23} atoms/mole$. R is the gas constant, $62396.0\, torr\, cm^3 \,/\, K\, mole$ and T is the temperature in degrees Kelvin.

Thus for the neutral case, the amount of metal entering the silicon dioxide from the overlying metal film is that predicted by the ideal gas law. Substituting the above constants into Eqn. (1.10) and rearranging results in

$$[M_{ox}] = 9.653 \times 10^{(B+18)} e^{\frac{-(E_{int} + Ak\ln 10 - (kDT^2 \times 10^{-3} \ln 10) - kT(C-1)\ln T)}{kT}} \tag{1.11}$$

which is plotted in Fig. [1.5] for various metals.

2. Singly Ionized Diffusors

To find the solid solubility for singly ionized diffusors the following reaction equations must be solved:

$$M_{sol} \leftrightarrows M_{gas} \qquad \Delta H_{sub} \tag{1.12}$$

$$M_{gas} \leftrightarrows M^{+}_{gas} + e^{-}_{gas} \qquad \Delta E_{ion} \tag{1.13}$$

$$M^{+}_{gas} \leftrightarrows M^{+}_{ox} \qquad \Delta E_{image} + \Delta E_{binding} + \Delta E_{other} \tag{1.14}$$

$$e^{-}_{gas} \leftrightarrows e^{-}_{ox} \qquad \Delta E_{image} + \chi + \Delta E_{other} \tag{1.15}$$

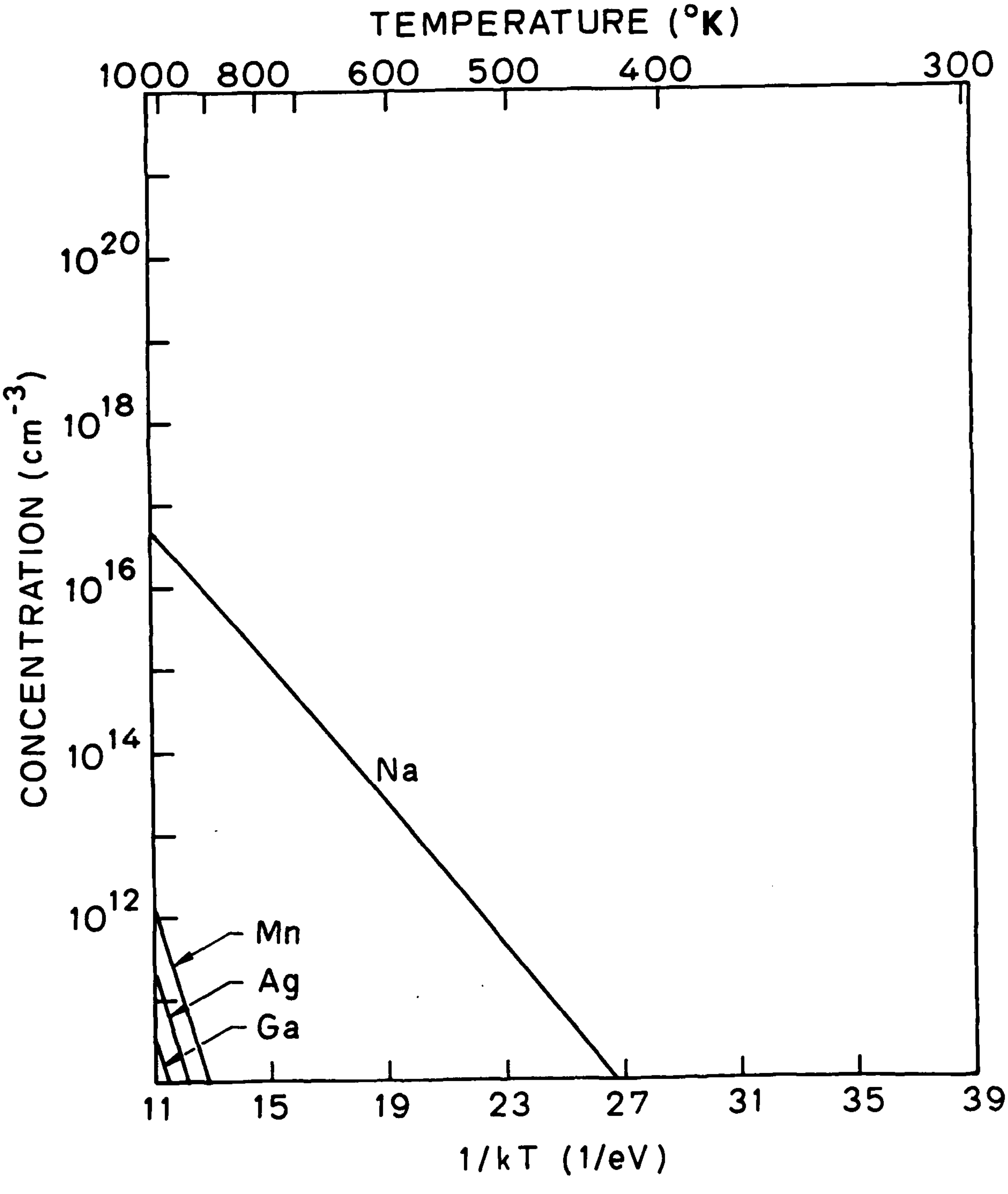

Figure 1.5. Interstitial Diffusion of Neutral Atoms. Solid solubility calculations for the interstitial diffusion of neutral atoms. Pd,Mo,Fe,Au,Cu,Ta,W,Ni and Pt have solid solubilities less than $10^{10} cm^{-3}$.

In the above equations the heat of formation for each reaction is shown to the right of each equation. ΔH_{sub} is the heat of sublimation and is known for all elements, [1.3, 1.4]. ΔE_{ion} is the ionization potential and is also known for most elements, [1.3, 1.4]. $\Delta E_{binding}$ is found as described in section 2*b*. χ is the electron affinity. ΔE_{image} is the image charge for both the positive ion and the negative electron. ΔE_{other} is any other heat of formation, such as a catalyst to the diffusion process.

Combining all the unknown heats of formations into one term, $E_{remainder}$, gives

$$\Delta E_{remainder} = 2\Delta E_{image} + 2\Delta E_{other} + \chi \qquad (1.16)$$

Combining the above reaction equations results in

$$M_{sol} \leftrightarrows M_{ox}^{+} + e_{ox}^{-} \qquad \Delta H_{sub} + \Delta E_{ion} - \Delta E_{binding} - \Delta E_{remainder} \qquad (1.17)$$

for the metal solid solubility for the singly ionized diffusor.

We can deal with this equation in a manner similar to the neutral case, which gives the following expression for the solid solubility of singly ionized atoms in SiO_2 (See Fig. [1.6]).

$$[M_{ox}^{+}] = 1.527 \times 10^{\left(\frac{B}{2}+17\right)} e^{\frac{-(E_{int} + kA\ln 10 - (kT^2 D \times 10^{-3} \ln 10) - \frac{kT}{2}(2C+1)\ln T)}{2kT}} \qquad (1.18)$$

3. Doubly Ionized Diffusors

For doubly ionized diffusors we can derive the following reaction equation

$$M_{sol} \leftrightarrows M_{ox}^{++} + 2e^{-} \qquad \Delta H_{sub} + \Delta E_{ion} + 2\Delta E_{remainder} \qquad (1.19).$$

In this derivation we have assumed that the unknown remainder heat of formation is twice that of the singly ionized case. Applying the law of mass action in a manner similar to the previous two cases results in

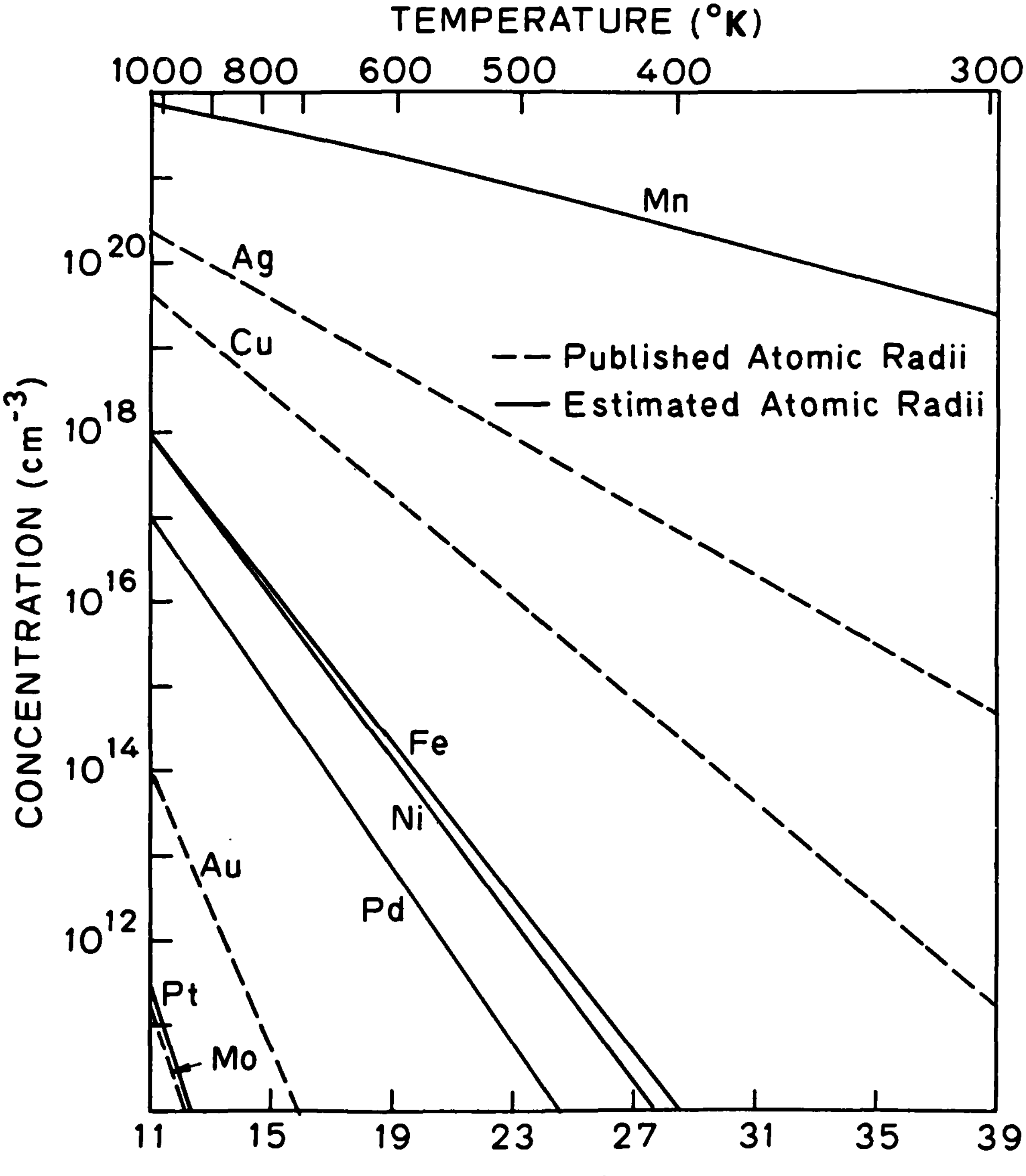

Figure 1.6. Singly Ionized Solid Solubility. Calculated solid solubility for singly ionized atoms. Ga and Na have values $\succ 10^{22} cm^{-3}$ while Ta and W have values $\prec 10^{10} cm^{-3}$.

$$\frac{[M_{gas}]}{[M_{ox}^{++}][e^-]^2} = e^{-\chi_{gas} - \chi_{M_{ox}^{++}} - 2\chi_{e^-}} \tag{1.20}$$

where χ for each species is defined in Appendix B. We also know that

$$[M_{ox}^{++}] = 2[e^-] \tag{1.21}.$$

Combining these equations and reducing we obtain

$$[M_{ox}^{++}] = 4[M_{gas}]^{\frac{1}{3}}\left(\frac{2\pi m_e kT}{h^2}\right)e^{\frac{-E_{int}}{3kT}} \tag{1.22}.$$

Where E_{int} is the internal energy of each species

$$\Delta E_{int} = 2\Delta E_{e^-} - \Delta E_{gas} - \Delta E_{M_{ox}^{++}} \tag{1.23}$$

or

$$E_{int} = \Delta E_{ion} - \Delta E_{binding} - 2\Delta E_{remainder} \tag{1.24}$$

The solid solubility for the doubly ionized case is then

$$[M_{ox}^{++}] = 6.084 \times 10^{(16+\frac{B}{3})} e^{\frac{-(E_{int} + kA\ln 10 - (kT^2 D \times 10^{-3}\ln 10) - kT(c+2)\ln T)}{3kT}} \tag{1.25}$$

and is plotted in Fig. [1.7]

4. Triply Ionized Diffusors

The solid solubility of the triply ionized diffusors, $[M_{ox}^{+++}]$, is found using an approach similar to the other cases and results in.

$$[M_{ox}^{+++}] = 27[M_{gas}]^{\frac{1}{4}}\left(\frac{2\pi m_e kT}{h^2}\right)^{\frac{9}{8}} e^{\frac{-E_{int}}{4kT}} \tag{1.26}.$$

Assuming that the unknown heat of formation is three times that of the singly ionized case. We obtain

$$\Delta E_{int} = \Delta E_{ion} - \Delta E_{binding} - 3\Delta E_{remainder} \tag{1.27}$$

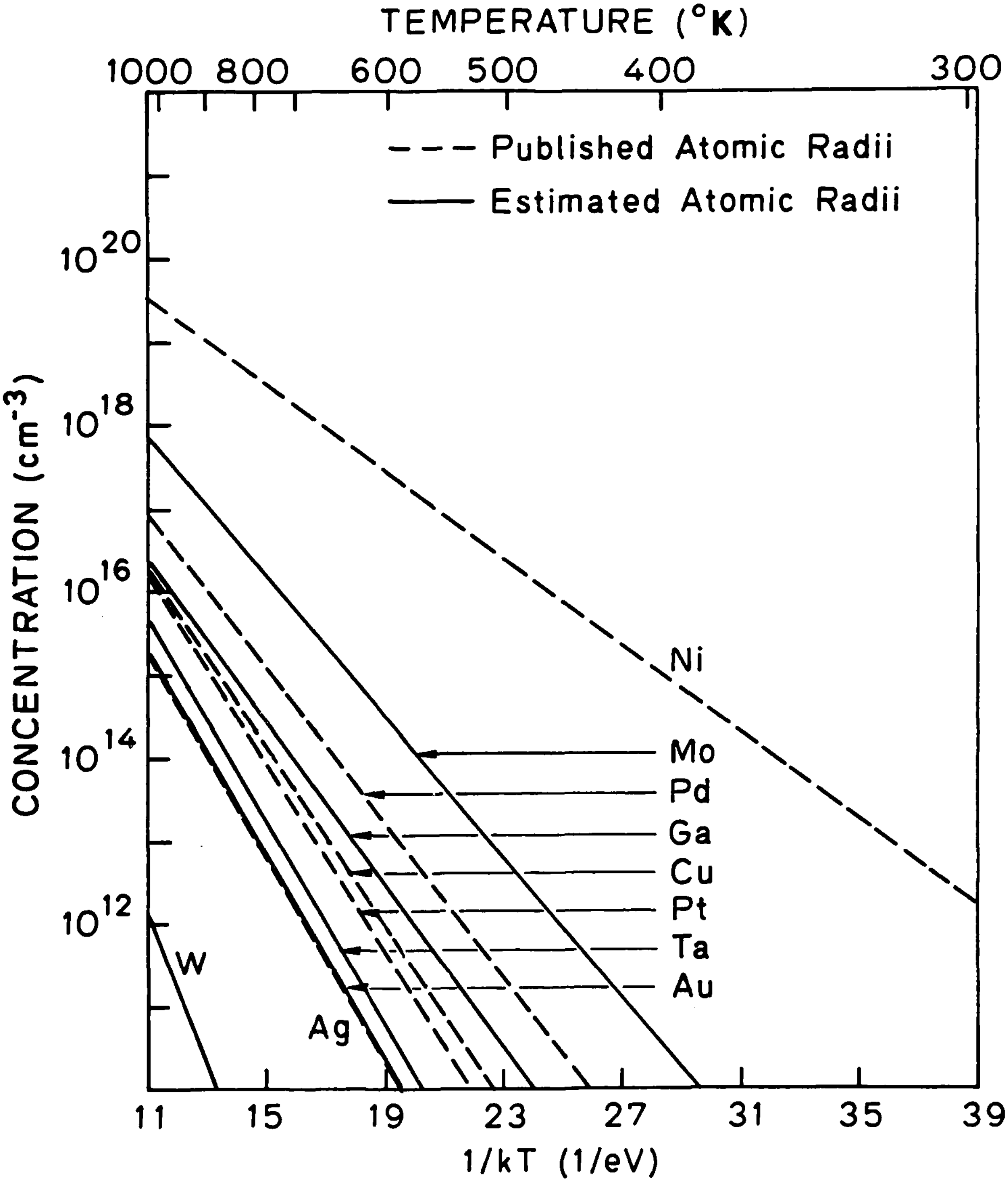

Figure 1.7. Doubly Ionized Solid Solubility. Calculated solid solubility for doubly ionized atoms. Mn and Fe have values $\succ 10^{22} cm^{-3}$ while Na has a value below $10^{10} cm^{-3}$.

or in terms of each species

$$\Delta E_{int} = 3\Delta E_{e^-} + \Delta E_{M_{ox}^{+++}} - \Delta E_{gas}. \tag{1.28}$$

Substituting known values results in

$$[M_{ox}^{+++}] = 4.38 \times 10^{(16+\frac{B}{4})} e^{\frac{-(E_{int} + Ak \ln 10 - (kT^2 D \times 10^{-3} \ln 10) - \frac{(2C+7)kT \ln T}{2})}{4kT}} \tag{1.29}$$

which has been plotted in Fig. [1.8].

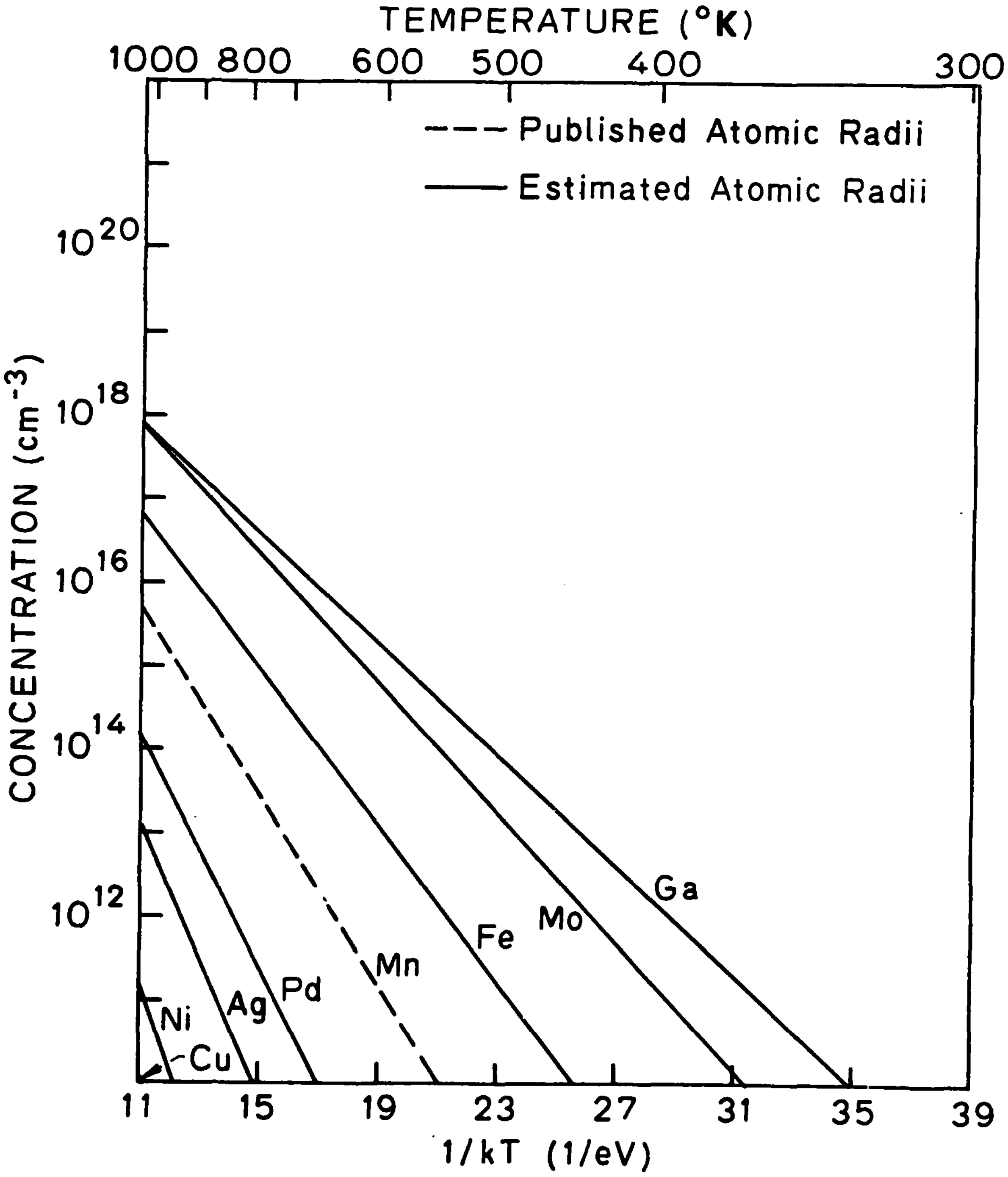

Figure 1.8. Triply Ionized Metal Solid Solubility in SiO_2. Calculation of the solid solubility of triply ionized metal atoms. Na has a value $\prec 10^{10} cm^{-3}$. No other atoms were calculated due to lack of published information.

In general the solid solubility takes on the form of

$$C_{sol} = C_o e^{\frac{-E_{effective}}{kT}} \tag{1.30}$$

for all cases. A negative value for $E_{effective}$ implies that the atom in question would rather be in the oxide than out. Values for $E_{effective}$ for various elements are found in Appendix A.

5. Calibration of Solid Solubility Calculations

The figures shown in this chapter were based on a value for $\Delta E_{remainder}$ calculated from the measured solid solubility of silver in silicon dioxide. This calculation assumes that all of the silver in the oxide was put there while in a singly ionized state. In light of the data presented earlier which showed no detectable diffusion for unbiased samples this is quite reasonable.

Using an upper bound , as observed with RBS, of $[Ag_{ox}] = 3 \times 10^{18} cm^{-3}$, we find $\Delta E_{remainder} = 8.87eV$. Using this value in the following equation

$$\Delta E_{effective} = \frac{E_{int} + kAln10 - (kT^2 D \times 10^{-3} ln10) - \frac{kT}{2}(2C+1)lnT}{2} \tag{1.31}$$

we obtain a value for $\Delta E_{effective}$ of approximately $0.5eV$ for singly ionized silver in SiO_2.

For the doubly and triply ionized cases $\Delta E_{remainder}$ was taken to be $9eV$ since we can't be sure of the exact values without more accurate data for the ionized radii, image charge, etc. However, these values allow us to see trends of the solid solubilities in silicon dioxide and should be close to the actual values. In the following chapter we compare this model with actual experiments to test its validity.

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Chapter II
EXPERIMENTAL ANALYSIS

In this chapter a simplified expression for the diffusion equation which allows extraction of the diffusion coefficient from experimental data is developed. The extracted diffusion coefficients and the observed activation energies are then compared with the values predicted by the theory developed in chapter I.

A. Solution of Diffusion Equation

A complete solution to the diffusion equation is given in Appendix C and Ref. [2.1]. In this section we present a solution to the diffusion equation that holds when the electric field, $\mathcal{E}$, dominates the diffusion process and still meets the following critria,

$$\mathcal{E} \ll \frac{kT}{qb} \approx T \times 10^{22} V/cm \qquad (2.1)$$

Then the flux can be written as (see Appendix C)

$$J = q\mu C_{sol}\mathcal{E} - D\frac{\delta C}{\delta x} \qquad (2.2).$$

In this equation q is the charge of an electron, b is the distance between potential barriers, about 5 Å. μ is the mobility, $\mu = \frac{q}{kT}D$, C is the concentration and x is the distance into the silicon dioxide.

When the electric field term is large compared to the concentration gradient Eqn. (2.2) can be further reduced to

$$J = \frac{q}{kT}DC_{sol}\mathcal{E} \qquad (2.3).$$

In the following this equation is used to determine the diffusion coefficient since the other parameters are known.

1. Silver Diffusion

Using measured data on silver diffusion in silicon dioxide at $300°C$ we derive a flux for silver through silicon dioxide. This is done by dividing the amount of silver observed to pile up at the silicon/silicon dioxide interface during a BTS by the anneal time. In Fig. [2.1] we show how the amount of silver observed at the interface in $atoms/cm^2$ increases with time. The slope of this plot is the flux of silver through the silicon dioxide. The solid solubility of silver in silicon dioxide at $300°C$ was observed with RBS to be $3 \times 10^{18} cm^{-3}$ as an upper bound. Combining this number along with an electric field of $5.2 \times 10^4 \, V/cm$ and a flux of $1.43 \times 10^{12} cm^{-2}/sec$, see Fig. [2.1] we obtain by rearranging Eqn. (2.3)

$$D_{Ag} = 4.5 \times 10^{-13} cm^2/sec$$

at $300°C$.

Using measured silver diffusion data in silicon dioxide at various temperatures Fig. [2.2] can be drawn. The slope of this plot is the activation energy, $E-a$, for silver diffusion in silicon dioxide, E_a is approximately $1.24eV$.

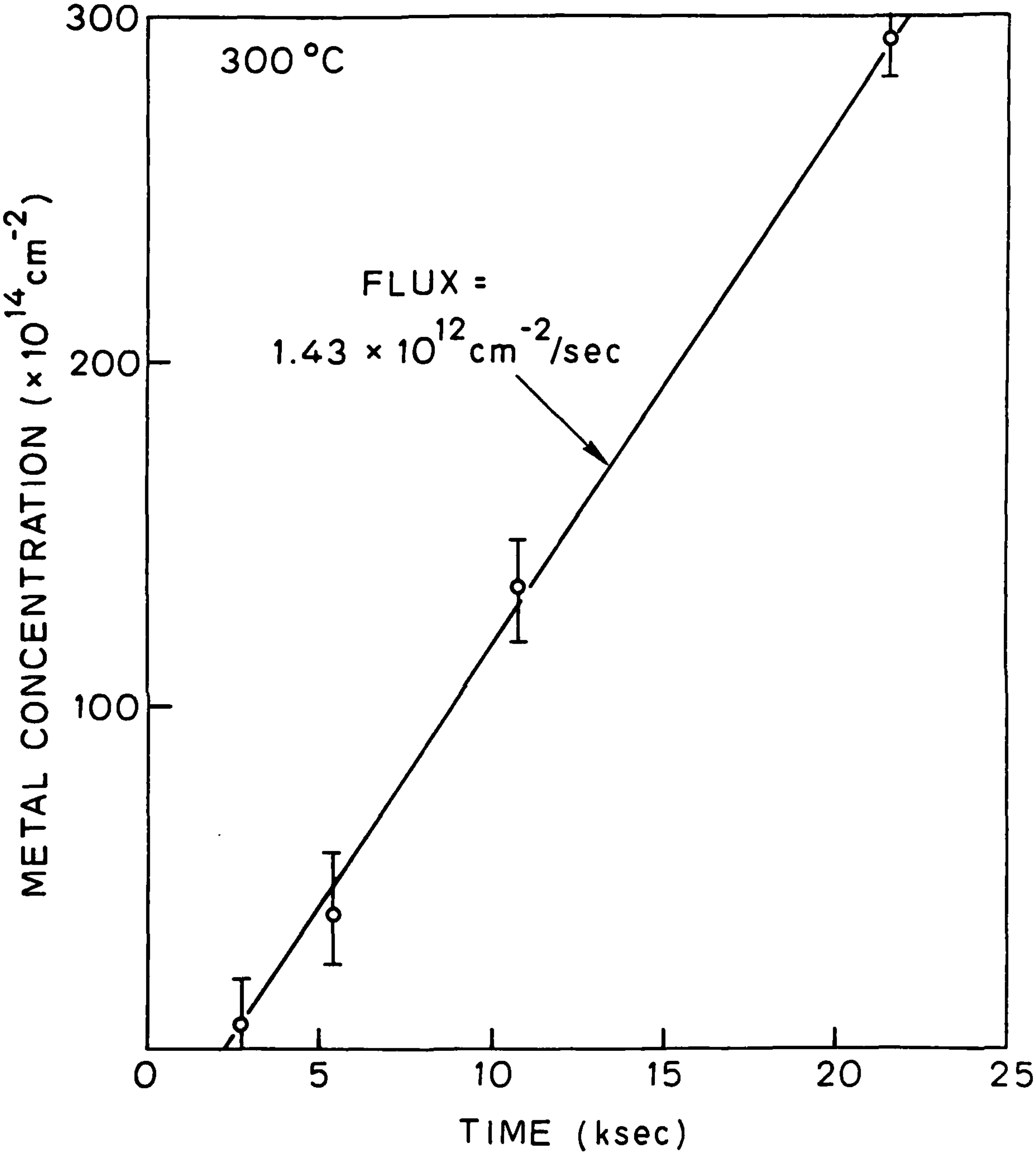

Figure 2.1. Silver Pile Up at the SiO_2/Si Interface versus Time.

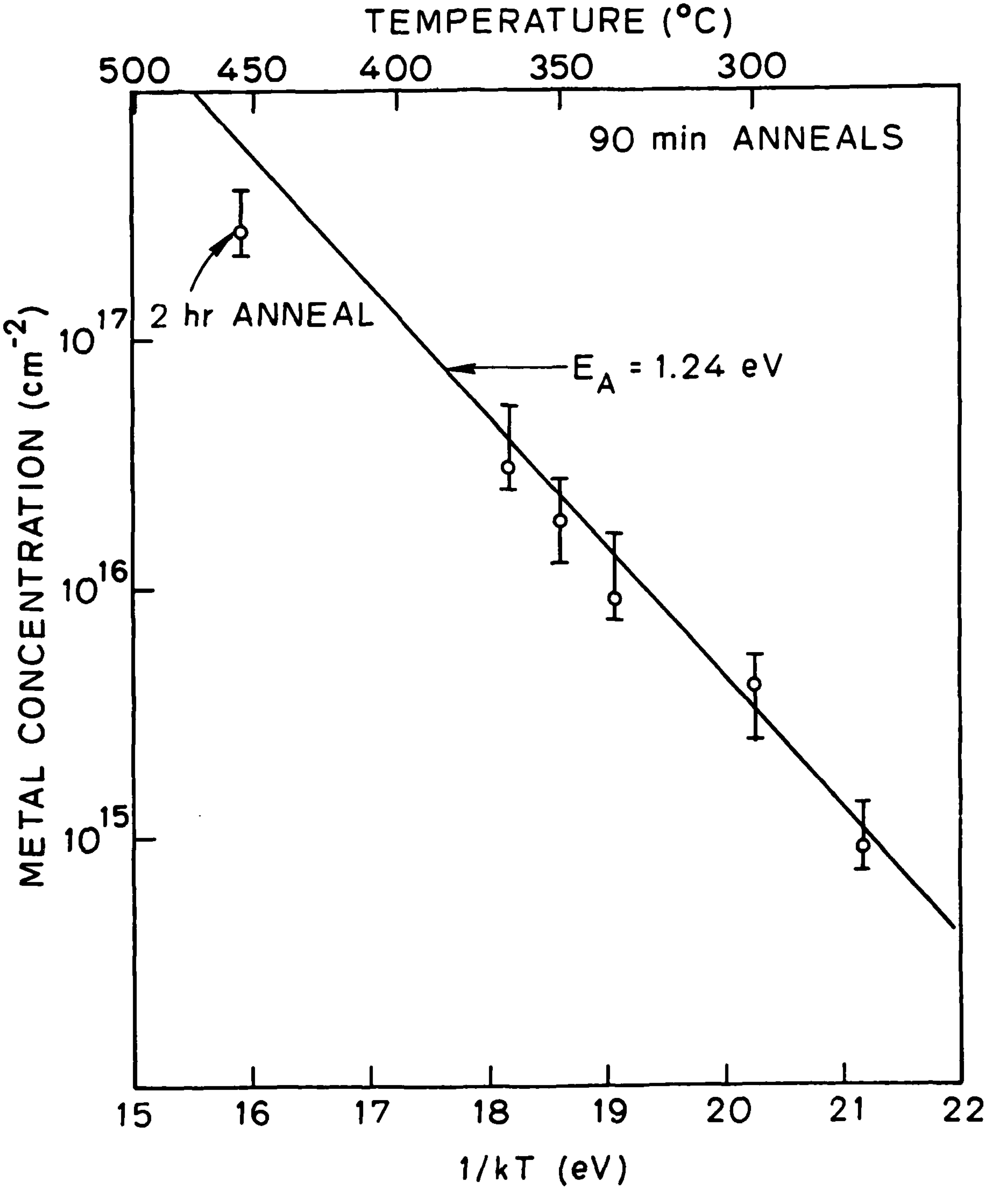

Figure 2.2. Silver Pile Up at the SiO_2/Si Interface versus Temperature.

a. Model versus Data

The model developed in Chapter I expresses the diffusion coefficient by Eqn. (1.1) and the solid solubility by Eqn. (1.30). Combining these two equations with Eqn. (2.3) we write the flux of atoms through the SiO_2 as

$$J = \frac{q}{kT}\mathcal{E} D_o C_o e^{\frac{-(E_{diffusion} + E_{solidsolubility})}{kT}} \quad (2.4)$$

We see from the above equation that the observed activation energy is equal to the sum of the activation energies defined in Chapter I. From Chapter I the predicted activation energy for diffusion is $1.3eV$ and the predicted solid solubility activation energy is $0.5eV$. The sum of $1.8eV$ is to be compared with that observed of $1.24eV$.

Evaluating Eqn. (1.1) at $300°C$ for silver results in

$$D_{Ag}^{predicted} = 0.025e^{-\frac{1.3}{kT}} = 9.2 \times 10^{-14} cm^2/sec \quad (2.5)$$

which is to be compared with our observed value at $300°C$ of $D_{Ag} = 4.5 \times 10^{-13} cm^2/sec$. We will reserve further discussion on these comparisons for the discussion section.

2. Copper Diffusion

To calculate the diffusion coefficient for copper we use the model developed in Chapter I to estimate the solid solubility of singly ionized copper in silicon dioxide at $450°C$ to be $1 \times 10^{18} cm^{-3}$. This assumption is necessary since the solid solubility of copper in silicon dioxide is below the detection limit of the RBS. This number should be a high estimate and therefore will give us the worst case answer. This approach also assumes that all the copper in the SiO_2 is singly ionized. Using the observed data for copper we can make plots similar to Figs. [2.1, 2.2]

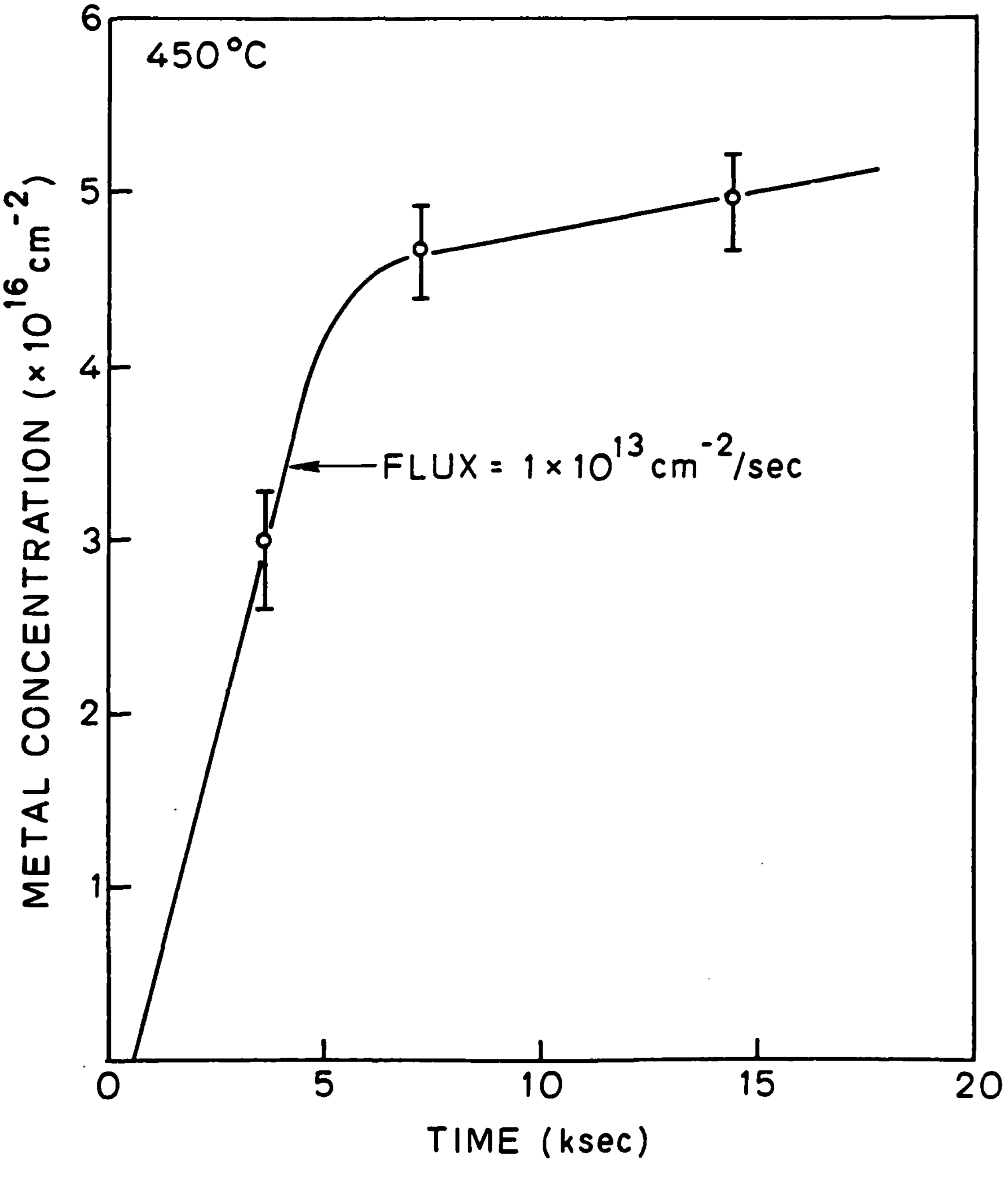

Figure 2.3. Copper Pile Up at the SiO_2/Si interface versus Time.

for determining the copper activation energy and copper flux through the silicon

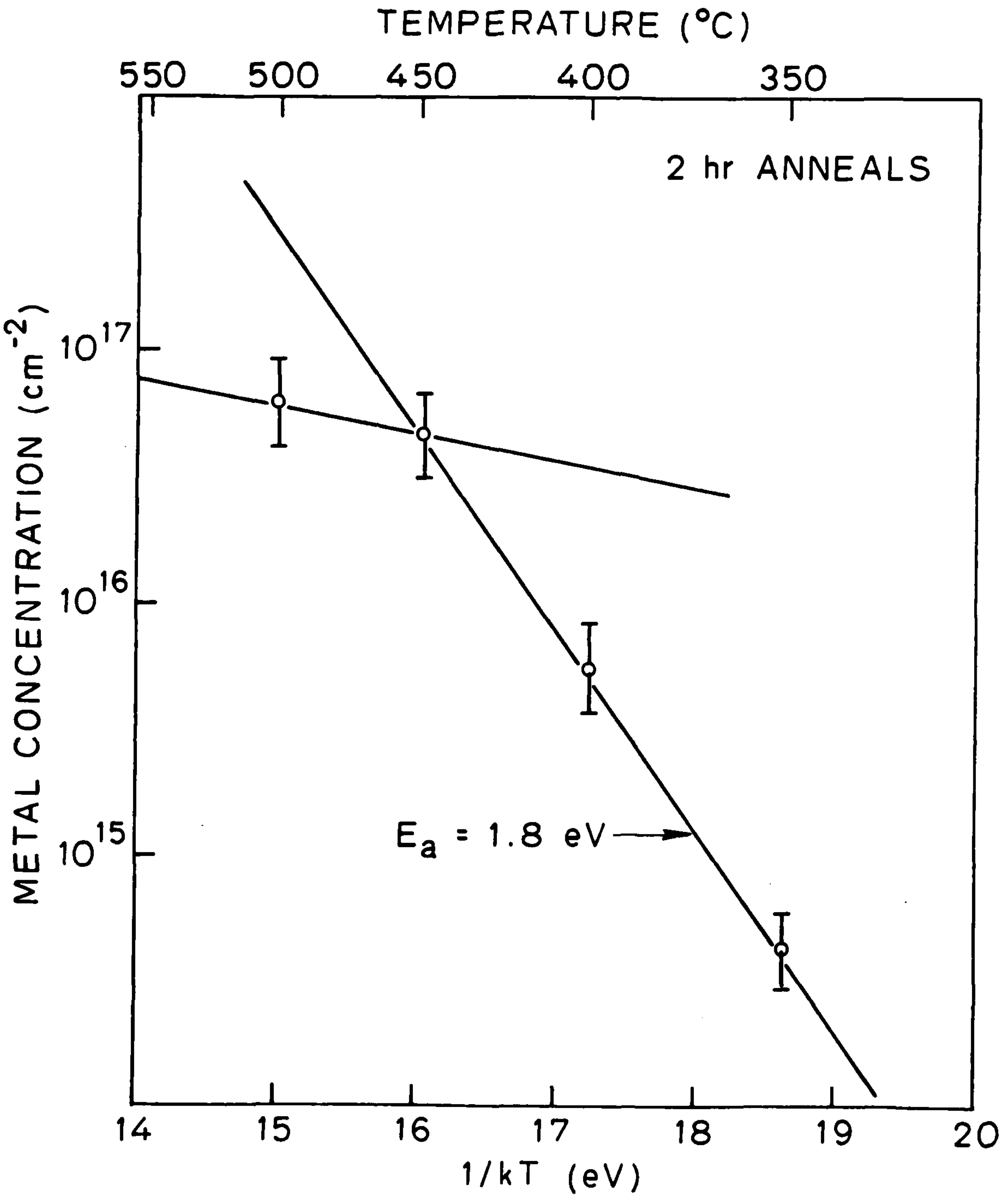

Figure 2.4. Copper Pile Up at the SiO_2/Si interface versus Temperature.

dioxide, see Figs. [2.3, 2.4].

We attribute the saturating of the data to the oxidation of the copper during BTS. After the copper has oxidized to the Cu/SiO_2 interface we lose both adhesion and electrical contact resulting in loss of the field aided diffusion. Before oxidation of the copper dominates, we find the observed activation energy to be $1.8 eV$ and the flux of copper atoms through the silicon dioxide at $450°C$ to be approximately $1.0 \times 10^{13} cm^{-2}/sec$. Equation [2.3] can be used to calculate the diffusivity of copper in silicon dioxide at $450°C$ with an electric field of $\mathcal{E} = 5.2 \times 10^4\, V/cm$, resulting in

$$D_{cu}(450°C) = \frac{\frac{kT}{q} J}{C_{sol}\mathcal{E}} = 1.2 \times 10^{-11} cm^2/sec \qquad (2.6).$$

a. Model versus Data

The result of Eqn. (2.6) is in reasonable agreement with the value of copper diffusion at $450°C$ predicted by Eqn. (1.1)

$$D_{Cu}^{predicted} = 0.025 e^{\frac{-1.2}{kT}} = 1.2 \times 10^{-10} cm^2/sec \qquad (2.7)$$

Summing the diffusion activation energy, $1.2eV$, and the solid solubility activation energy, $0.64eV$, results in the total activation energy, $1.84eV$, which compares nicely with the observed value of $1.8eV$.

3. Palladium, Gold and Titanium Diffusion

The diffusion of gold and palladium in silicon dioxide was undetectable using both C-V and RBS techniques. This was expected in light of our model which predictes a very low solid solubility in SiO_2 for these metals. Thus both palladium and gold are potential candidates for low temperature processing.

Titanium was found to react with silicon dioxide forming a Titanium oxide compound and is therefore not expected to be an interstitial diffusor. This agrees with what was observed experimentally. Also since Titanium is quite reactive the model presented earlier is not expected to apply.

B. Discussion

A comparison between the experimental results and those predicted by our model is quite good. Excellant agreement is found for copper. A slight discrepancy was found in the case of silver in that the theory predicts a lower diffusivity. In light of experiments that revealed the catalytic behavior of the atmosphere in which the experiment takes place, we propose the following explanations:

(1)The strain component of our model could easily be modified by the presences of a molecule or atom which changes the effective window, (r_d) through which diffusion occurs. The presence of such molecules or atoms could also have an effect on the electrostatic energy. If they were charged they would be able to shield or enhance this effect and change the activation energy from that predicted by our model.

(2)These molecules or atoms could also modify our description of the solid solubility by adding another heat of formation into the equations. If we consider the silicon dioxide as having a band gap then the addition of a molecule or atom into SiO_2 changes the Fermi energy. This change in the Fermi energy may lower the ionization energy of the metal atoms and therefore change the solid solubility.

This comparison of our model with experimental data illustrates the usefulness of this approach. More work is needed before this model is completely quantitative. In its present state, however, it can be used to predict which metals are likely candidates for VLSI applications and which are not. In the next chapter we explore the implications and trends predicted by this model.

References

Chapter II

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Chapter III
IMPLICATIONS AND CONCLUSIONS

In this chapter recommendations for metals which maybe used successfully for VLSI applications are presented. Reasons for these conclusions are also presented. Futher results of experiments, not yet documented, are presented in support of these predictions.

A. Implications

To determine which metals are viable candidates for VLSI we need to define a criteria to compare each metal against. In the sections that follow we use the number of metal atoms found at the SiO_2/Si interface or an equivalent as our means of comparison. Further, we define an integrated area of $10^{10} cm^{-2}$ or greater as the point of failure for a metal at a given temperature.

We present the neutral, singly, doubly and triply ionized cases for most of the atoms listed in Appendix A. For some atoms it is obvious that the present approach doesn't apply. Discussion of these discrepancies will occur later.

1. Neutral Case

For the neutral case we solve Eqn. (2.2) with $\mathcal{E} = 0$ and the following boundary conditions:

$$C(0,t) = C_s$$

$$C(\infty, t) = 0 \tag{3.1}$$

$$C(x, 0) = 0.$$

Where C is the concentration and C_s is the solid solubility.

The solution is

$$C(x,t) = C_s\, erfc\left[\frac{x}{2(Dt)^{\frac{1}{2}}}\right] \tag{3.2}.$$

where C_s is given by Eqn. (1.30), D, the diffusion coefficient, is given by Eqn. (1.1) and t is the time in seconds.

To get from this equation to our definition for failure we must integrate from x to infinity. Here x is the location of a fictitious silicon/silicon dioxide interface. This gives us

$$C_{N_t} = C_s\left[2\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} e^{\frac{-x^2}{4Dt}} - x\, erfc\left[\frac{x}{2(Dt)^{\frac{1}{2}}}\right]\right] \tag{3.3}.$$

The above equation yields the number of atoms which have passed the point x in a semi-infinite slab of silicon dioxide. This simplified view represents the case where the metal atoms pile up at the SiO_2/Si interface or diffuse into the silicon substrate but do not interfere with the diffusion process. The value for x is the silicon dioxide thickness that we wish to consider. Figure [3.1] is a plot of this equation versus temperature for an oxide thickness of 1000 Å and a time of 1 year. It can be seen that all the atoms considered do not cause any failures, as we have defined failure, until very high temperatures. Figure [3.2] is a similar plot, however the time is 10 years. We observe only a slight increase in the number of neutral atoms that passed through the silicon dioxide for the ten year case versus the one year case. This result implies that for the neutral case, the solid solubility dominates the diffusion process in the silicon dioxide. The metal concentration reaches solid solubility rapidly and no further diffusion takes place. Fortunetly the solid solubilities for all most all metals is small enough not to rule any out as possible candidates for VLSI applications.

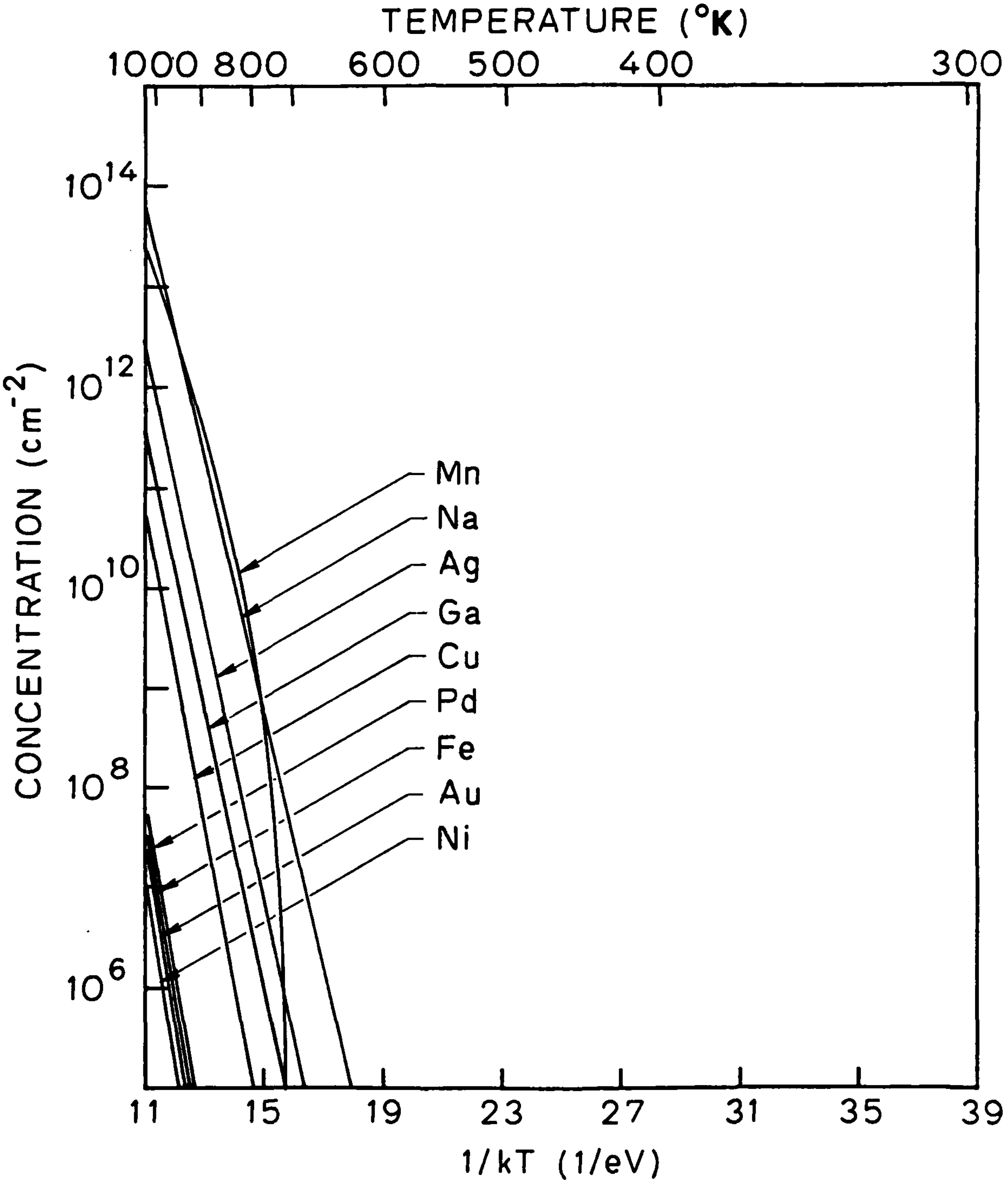

Figure 3.1. Number of Neutral Atoms Passed the Oxide after One Year. Calculated number of neutral atoms diffused through a 1000 Å oxide after 1 year.

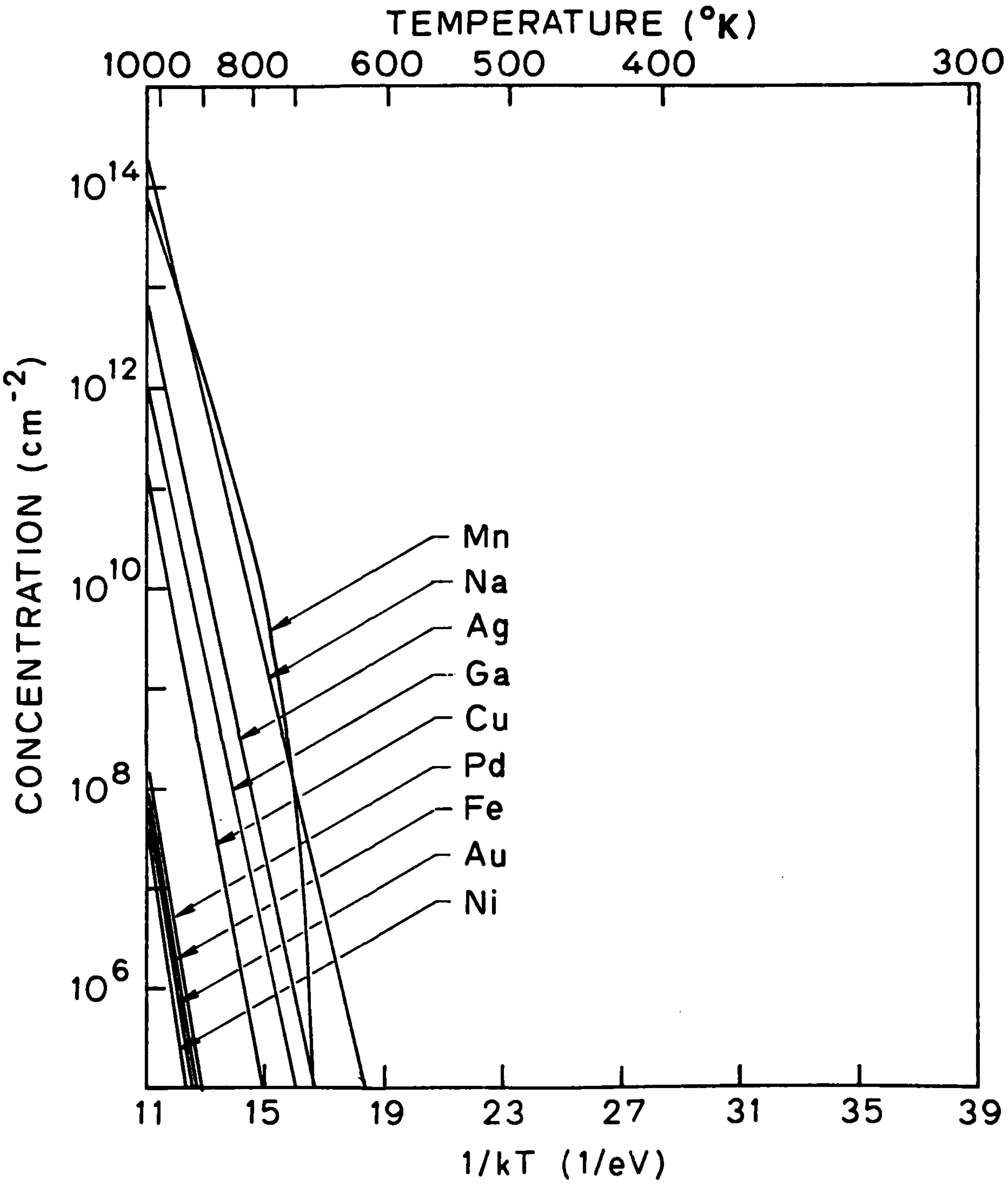

Figure 3.2. Number of Neutral Atoms Passed the Oxide after Ten Years. Calculated number of neutral atoms diffused through a 1000 Å oxide after 10 years.

2. Ionized Case

Equation (2.3) is used for the ionized case to predict a failure. Using the same definition of failure, i.e. $10^{10}\, atoms/cm^2$ or more that reach the interface for a given time and temperature, as in the neutral case. We rewrite Eqn. (2.3) as

$$C_{N_t} = \frac{q}{kT} D C \mathcal{E} t \qquad (3.4).$$

Where C_{N_t} is the number of atoms that reach the interface per square centimeter. D is the diffusion coefficient, Eqn. (1.1). C is the solid solubility, Eqn. (1.30). $\mathcal{E}$ is the electric field, $10^6\, V/cm$. T is the temperature, k is the Boltzmann constant and q is the charge on a electron. t is the time.

For the ionized case an additional criteria for failure is needed, the value of the electric field. We set the field at a value of $10^6\, V/cm$. Using this value for the electric field and one year for the time, Eqn. (3.4) is plotted against temperature, Figs. [3.3 – 3.5], to reveal the failure rate for ionized metal atoms diffusing in SiO_2. To evaluate failures after ten years or any other length of time, we simply multiple the values in these figures by the length of time in years.

These curves depend on the silicon dioxide thickness only in the determination of the effective electric field. Thus for this approach to be valid the solid solubility of each metal must be reached quickly. The observed behavior of copper and silver support this assumption.

Figure [3.3], the singly ionized case, predicts the most failures. Those atoms that ionize easily should be considered very carefully before using in VLSI applications. Metals to the left of and including palladium in Fig. [3.3] should be safe for for VLSI applications.

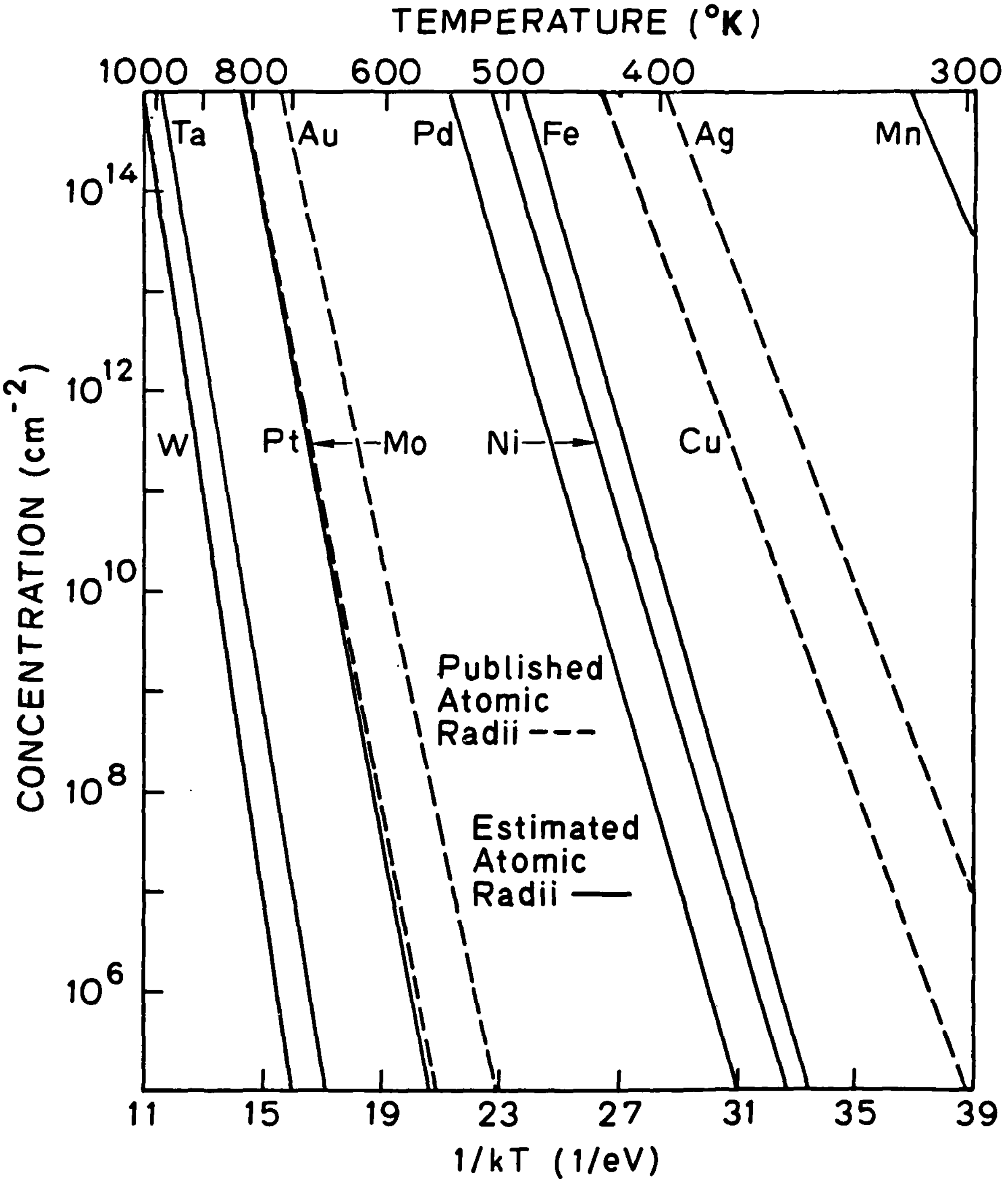

Figure 3.3. Singly Ionized Atoms that have Reached the SiO_2/Si Interface after One Year. Calculated failure rate of singly ionized atoms after one year. Na and Ga have values $\succ 10^{15} cm^{-2}$.

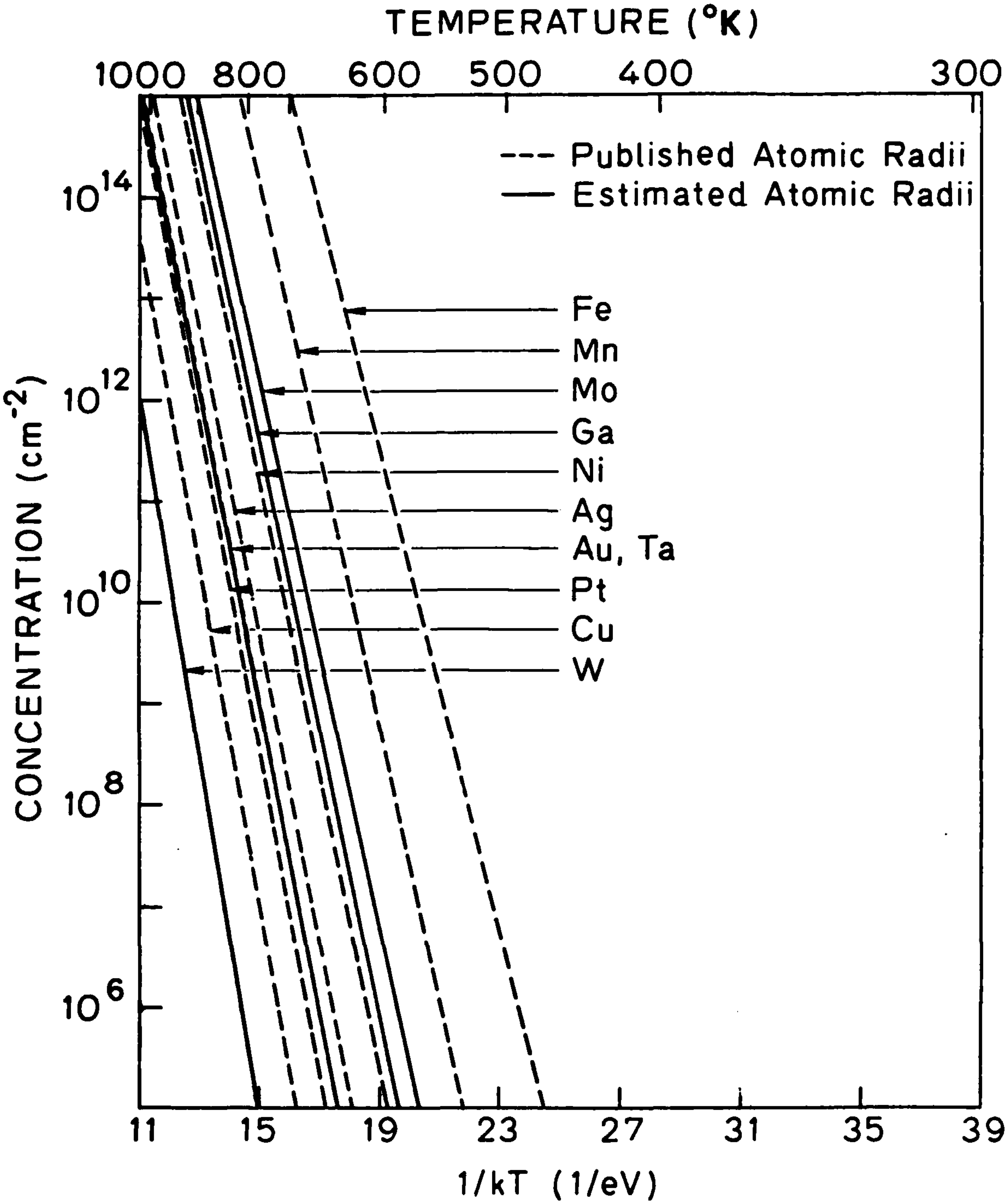

Figure 3.4. Doubly Ionized Atoms that have Reached the SiO_2/Si Interface after One Year. Calculated failure rate of doubly ionized atoms after one year. The value for Na is $\prec 10^5 cm^{-2}$.

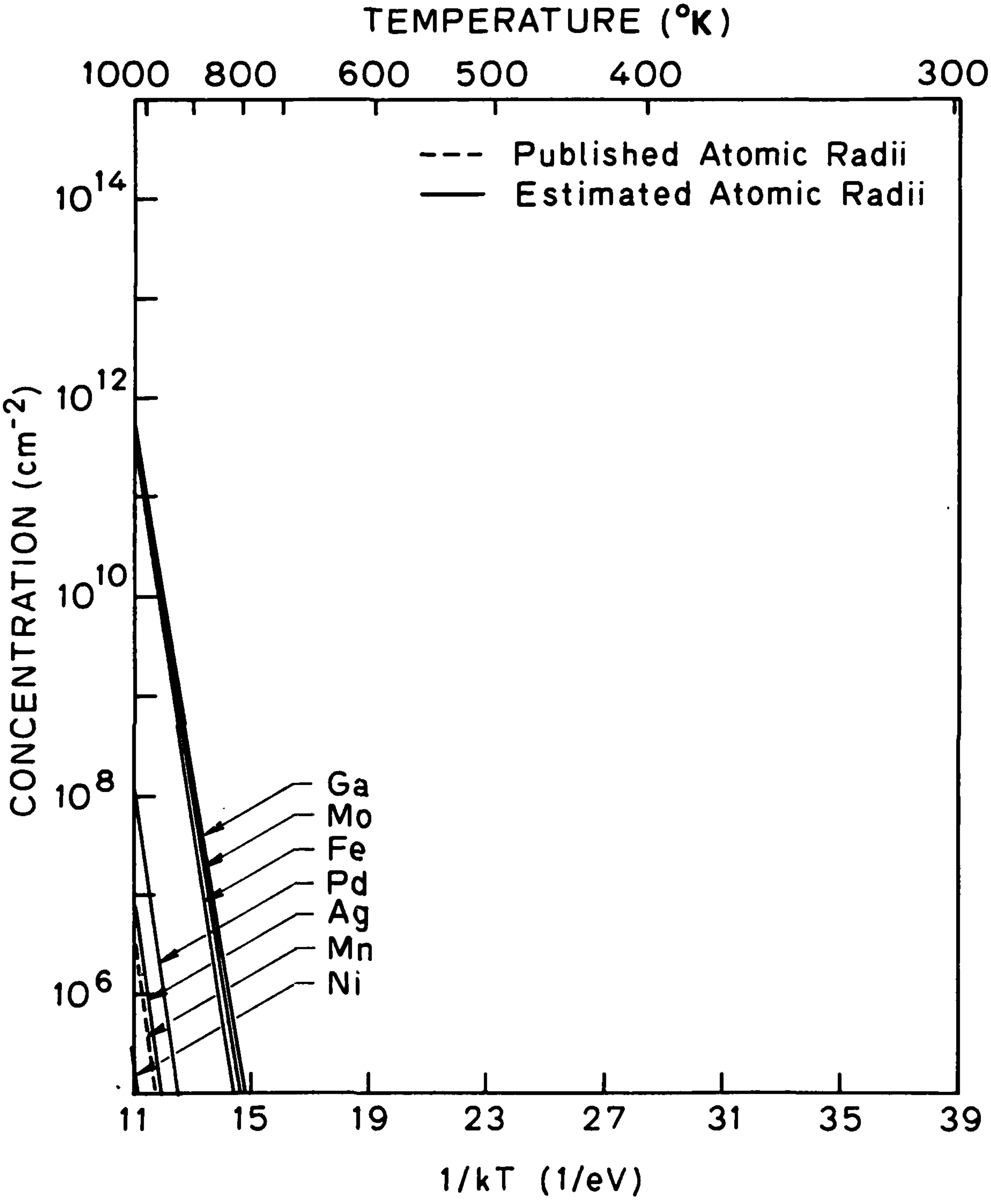

Figure 3.5. Triply Ionized Atoms that have Reached the SiO_2/Si Interface after One Year. Calculated failure rate of triply ionized atoms after one year. Cu and Na have values $\prec 10^5 cm^{-2}$.

B. Other Considerations

The model presented so far only predicts the diffusion and solid solubility of atoms in and through silicon dioxide. There are two major considerations that can dominate and invalidate the present approach. The first consideration is when the atom in question reacts with the silicon dioxide and the second consideration is whether the atom reacts with any other substances present.

Examining the atoms found in Appendix A. we see that both titanium and aluminum reduce silicon dioxide. This reaction is the reason that aluminum has worked so well as a metallization system. Arsenic, phosphorus, boron and sodium are know network formers in silicon dioxide [3.1 –3.5] and therefore diffuse by methods different than those presented in this work.

All of the atoms we have considered, except for gold and platinum, form stable oxides. Oxidation of the diffusing atom will obviously cause a change in the predicted diffusivity and solid solubility. The data for copper is a vivid example. Another example is manganese which oxidized so rapidly that continuity of the electric field was lost very quickly. Even so manganese reached levels detectable by RBS in the silicon dioxide, in further support of our model.

The reaction of the diffusing atom with any substance will also alter its predicted behavior. It is believed that a reaction of some diffusing atoms with water molecules has a catalytic enhancement on the diffusion of these atoms. Once an understanding of this reaction is obtained it can be easily incorporated into our model.

In addition to the above considerations, a metal that is to be considered for VLSI applications must also have good adhesion, be easily etched, delineated, form ohmic contacts with silicon and be easily applied.

1. Conclusions

From this study in can be concluded that Pd, Au, Mo, Ta, W, Pt, Ti, and Al are potential candidates for VLSI metalization.

It is possible that gold should be eliminated due to its well known diffusion in silicon. Others aspects, such as adhesion, low contact resistance and easy chemical processing should also be considered before any final choice is made.

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Chapter III

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3.4. C. T. Sah et. al., "Diffusion of Phosphorus in Silicon Oxide Film", J. Phys. Chem. Solids, Pergamon Press, vol. 11 1959, pages 288-298.

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APPENDIX A

A. Material Parameters

In this section the material parameters used in the interstitial diffusion model are presented as well as summary tables of the copper and sliver data.

Table A.1.

Silver Pile Up at 300°C.

Diffusion of silver through silicon dioxide by the pile up of silver at the interface.

Δ time (sec)	time (sec)	Area @ Interface (cts)	$H_{Si}^{SiO_2}$ (cts)	$(N_t)_{Ag}$ (cm^{-2})	$(N_t)_{Ag}$/time (cm^{-2}/sec)
	2700	660	1100	7.99×10^{14}	2.96×10^{11}
2700					1.19×10^{12}
	5400	3000	1025	3.98×10^{15}	1.33×10^{12}
5400					1.75×10^{12}
	10800	10640	1060	1.34×10^{16}	1.24×10^{12}
10800					1.47×10^{12}
	21600	24234	1100	2.93×10^{16}	1.36×10^{11}

Table A.2.

Silver Pile Up at the Interface for Various Temperatures.

90 minute anneals

temp °C	Area @ Interface (cts)	$H_{Si}^{SiO_2}$ (cts)	$(N_t)_{Ag}$ (cm^{-2})	1/kT (eV)
275	598	960	8.8×10^{14}	21.18
300	2375	1029	3.98×10^{15}	20.25
			$\sigma = 9.1 \times 10^{14}$	
335	6167	1081	8.95×10^{15}	19.09
			$\sigma = 4.3 \times 10^{15}$	
350	15936	1088	1.84×10^{16}	18.63
			$\sigma = 5.65 \times 10^{15}$	
365	32182	1068	3.06×10^{16}	18.19
			$\sigma = 5.11 \times 10^{15}$	
455	24200	1090		15.94

Table A.3.

Copper Pile Up at SiO_2 Interface.

450°C with a positive electric field of $5 \times 10^4\ V/cm$.

Δ time (sec)	time (sec)	Area @ interface (cts)	$H_{Si}^{SiO_2}$ (cts)	$(N_t)_{cu}$ (cm^{-2})	$(N_t)_{cu}$/time (cm^{-2}/sec)
	3600	9765	1194	2.99×10^{16}	8.32×10^{12}
3600				1.50×10^{16}	4.17×10^{12}
	7200	14525	1139	4.67×10^{16}	6.49×10^{12}
7200				2.83×10^{15}	3.93×10^{11}
	14400	15413	1162	4.86×10^{16}	3.38×10^{12}

Table A.4.

Copper Interface Pile Up With Temperature.

Copper silicon/silicon dioxide interface pile up at various temperatures.

temp °C	Area @ Interface (cts)	$H_{Si}^{SiO_2}$ (cts)	$(N_t)_{cu}$ (cm^{-2}	1/kT (eV)
400	1621	1083	5.48×10^{15}	17.24
450	14525	1139	4.67×10^{16}	16.05
500	18679	1111	6.16×10^{16}	15.01
350	230	1111	4.29×10^{14}	18.63

Table 5.

Material Parameters.

	Al	TiB	Ag	Au	Cu	Mo	Na	Pd	Ta	W	Ni	P+	Mn	Fe	Ga	As4	P4	B
Heat of Sublimation (eV)	3.41	4.88	2.97	3.83	3.52	6.83	1.0	3.95	8.10	8.81	4.46	5.86	2.89	4.31	2.86	3.14	3.44	5.92
Oxide Reduction	yes	yes	no	no	no	no	no	no	no	no	no	no	no	no	no	no	no	no
(Kcal)	-69.5	-70	+95		+62		+3.1	+80	+12.6	+69			+21					+5.5
Metal Oxidation	yes	yes	yes	no	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	yes	yes	no	yes
(Kcal)			-6.0		-40			-20.4			-58							
Atomic radii (Å)	1.41	1.465	1.442	1.439	1.276	1.40	1.915	1.373	1.47	1.41	1.245	1.385	1.25	1.26	1.35	1.25	1.08	--
Singly ionized radii			1.26	1.37	0.96	0.93	0.95											
Doubly ionized radii			0.89		0.72			0.80			0.69	0.80	0.80	0.74				
Triply ionized radii				0.85									0.66					

Table 6.

Material Parameters.

Vapor Pressure (torr)	Al	Ti_s	Ag	Av	Cu	Mo	Na	Pd	Ta	W	Ni	P+	Mn	Fe	Ga	As_4	P_4	B
$p = 10^B T^C e^{-(A/T)\ln 10 + DT\times 10^{-3}\ln 10}$																		
Temperature Range	1200-2800	1155-M_p	298-1234	298-1336	298-1356	298-M_p	400-1200	298-M_p	298-M_p	298-M_p	298-M_p	298-M_p	993-1373	900-1812	M_p-B_p	600-900	317-553	1000-Mp
A	16450	24400	14710	19820	17870	34700	5700	19800	40800	44000	22500	29200	14850	21080	14700	6160	2740	29900
B	12.36	13.18	11.66	10.81	10.63	11.66	11.33	11.82	10.29	8.76	13.60	13.24	17.88	16.89	10.07	9.82	7.84	13.88
C	-1.023	-.91	-.755	-.306	-.236	-.236	-1.718	-.755	--	+.50	-.96	-.855	-2.52	-2.14	-.5	--	--	-1.0
D	--	--	--	-.16	-.16	-.145	--	--	--	--	--	--	--	--	--	--	--	--
Neutral	--	1.1	1.04	1.03	.67	--	--	.89	--	.97	.62	.91	.62	--	--	--	--	--
$Ed = E_{strain}$	.97	.78	.81	1.04	.48	.94	2.54	.68	1.11	.73	.43	.71	.48	.64	.83	.62	.34	--
Singly (Er = 8.87eV)																		
$Ed = E_{binding} + E_{strain}$	--	1.21	1.31	1.43	1.21	1.22	1.21	(1.2)	(1.2)	(1.2)	(1.2)	(1.2)	(1.2)	(1.2)	(1.2)	(1.2)	(1.2)	(1.2)
$E_{binding}$	--	--	.67	.56	1.02	1.06	1.03	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
$E_{int} = E_{ion} - E_{binding} - Er$	--	--	-1.97	-0.21	-2.17	-1.83	-4.76	(-1.54)	(-1.99)	(-1.89)	(-2.24)	(-0.87)	(-2.44)	(-2.00)	(-3.87)	(-0.06)	(+0.61)	(+1.89)
E_{ion}	5.96	6.82	7.574	9.22	7.724	7.10	5.138	8.33	7.88	7.98	7.633	9.0	7.432	7.87	6.0	9.81	10.484	8.296
E_{eff}	--	--	+.49	+1.85	0.64	1.97	-1.61	1.21	3.02	3.43	1.15	2.48	0.78	1.71	-0.48	0.55	0.54	3.95
Doubly (Er = 18eV)																		
$Ed = E_{binding} + E_{strain}$	--	2.24	2.32	(2.30)	2.77	(2.30)	(2.30)	2.56	(2.30)	(2.30)	2.87	2.56	2.56	2.70	(2.30)	(2.30)	(2.30)	(2.30)
$E_{binding}$	--	--	2.23	(2.20)	2.75	(2.20)	(2.20)	(2.20)	(2.20)	(2.20)	2.85	2.50	2.50	2.69	(2.20)	(2.20)	(2.20)	(2.20)
$E_{int} = E_{ion} - E_{binding} - Er$	--	--	1.25	(0.30)	0.09	(-4.05)	(27.09)	(-0.78)	(-4.00)	(-2.50)	-2.70	-1.94	-4.86	-4.51	(0.37)	(-1.57)	(-0.48)	(4.95)
E_{ion}	18.74	13.57	21.48	20.5	20.29	16.15	47.29	19.42	16.2	17.7	18.15	18.56	15.64	16.18	20.57	18.63	19.72	25.149
E_{eff}	--	--	+1.32	1.31	1.13	0.86	9.34	0.99	1.27	2.01	+.54	+1.23	0.61	0.10	1.02	-0.[illegible]	-.08	3.58
Triply E_{int} (Er = 27eV)	--	--	(4.22)	--	(6.23)	(-3.47)	(41.12)	(2.32)	--	--	(4.56)	--	2.20	(0.043)	(0.0)	--	--	--
$Ed = E_{binding}$	--	--	(3.60)	3.61	(3.60)	(3.60)	(3.60)	(3.60)	(3.60)	(3.60)	(3.60)	(3.60)	4.44	(3.60)	(3.60)	(3.60)	(3.60)	(3.60)
E_{ion}	--	27.47	34.82	--	36.83	27.13	71.715	32.92	--	--	35.16	--	33.64	30.643	30.6	--	--	--
E_{eff}	--	--	+1.69	--	+2.33	+0.74	+0.29	+1.46	--	--	+2.16	--	+1.25	+1.00	+0.62	--	--	--

APPENDIX B

A. General Theory of Reaction Equilibria

For the case of constant temperature and pressure the Gibbs free energy may be written as [B.1] ,

$$G = U - TS + PV \tag{B.1}$$

since it is at a minimum with respect to the proportions of the reactants. The incremental Gibbs energy may be written as [B.1],

$$dG = \sum_j \mu_j dN_j = dU \tag{B.2}$$

where μ_j is the chemical potential of species j and dN_j is the change in the number of molecules of species j.

The change in the Gibbs free energy in a reaction is seen to be closely related to the chemical potentials of the reactants [B.1]. In equilibrium this change must be zero for constant P and T.

$$dG = \sum_j \mu_j dN_j = 0 \tag{B.3}$$

The change, dN_j, in the number of molecules of species j is proportional to the number of moles of species j as determined by the balanced chemical equation of reaction. Let ν_j denote this coefficient and let A_j denote the chemical compound of species j. Then the balanced chemical equation can be written as

$$\sum_j \nu_j A_j = 0 \tag{B.4}$$

We can write dN_j as:

$$dN_j = \nu_j dN' \tag{B.5}$$

where dN' is the increment in the number of times the reaction takes place [B.1]. Combining Eqn. (B.3) and (B.5) results in:

$$dG = \sum_j \mu_j \nu_j dN' = 0 \tag{B.6}$$

simplifying

$$\sum_j \mu_j \nu_j = 0 \tag{B.7}$$

Equation (B.7) must be satisfied to be in equilibrium at constant temperature and pressure.

B. Law of Mass Action and Equilibrium for Idea Gases

If we assume that each constituent behaves like an idea gas, the chemical potential, μ_j, of identical polyatomic molecules is found as follows [B.1]:

Each molecule has rotational and vibrational motions so that the total energy, E_t, of a molecules' orbital t is the sum of two parts,

$$E_t = E_{int} + E_n \tag{B.8}$$

where E_{int} refers to the internal degrees of freedom and E_n to the translational motion of the center of mass of the molecule. For translational motion it can be shown [B.1] that

$$E_n = \frac{\hbar^2}{2m}\left(\frac{\pi n}{L}\right)^2 \tag{B.9}$$

where n is the quantum number of the translational orbital and L is the is integer times half a wave length. E_{int} includes the vibrational energy of the molecule on the force constant and the rotational energy of the molecule [B.1].

In the classical regime the probability that a given translational orbital, n, be occupied is always very small in comparison with one. When we write the grand sum of the orbital in this regime we may neglect terms in the λ^2 and higher powers of λ, because such terms correspond to occupancy of the orbital by more than one molecule.

Accordingly, the grand sum for the system of all orbitals, t, for which the translational quantum number is precisely n and for which the internal quantum number i assumes all possible values is

$$z = 1 + \lambda \sum_i e^{-(E_{int}+E_n)/kT} \tag{B.10}$$

since we're assuming the classical regime we may factor $e^{-E_n/kT}$ to obtain

$$z = 1 + \lambda e^{-E_n/kT} \sum_i e^{-E_t/kT} \tag{B.11}$$

Note that λ is the absolute activity, $\lambda \equiv e^{\mu/kT}$. We define

$$z_{int} = \sum_i e^{-E_{int}/kT} \tag{B.12}$$

as the partition function of all the internal degrees of freedom.

So equation (B.11) becomes

$$z = 1 + \lambda z_{int} e^{E_n/kT} \tag{B.13}$$

The probability that the translational orbital, n, is occupied irrespective of the state of internal motion of the molecule, is given by the ratio of the term in λ to the grand sum z.

$$f(E_n) = \frac{\lambda z_{int} e^{-E_n/kT}}{1 + \lambda z_{int} e^{-E_n/kT}} \approx \lambda z_{int} e^{-E_n/kT} \tag{B.14}$$

for the classical regime which holds when $f(E_n) \ll 1$.

If we now compare this result to that of an idea monatomic gas [B.1] we note that the only difference is the addition of the z_{int} term and λ becomes:

$$\lambda = e^{\mu_j/kT} = \frac{N}{V}\left(\frac{2\pi\hbar^2}{m_j kT}\right)^{\frac{3}{2}} \frac{1}{z_{int}} \tag{B.15}$$

and thus

$$\mu_j = kT\left[\frac{N}{V} ln\left(\frac{2\pi\,\hbar^2}{m_j kT}\right)^{\frac{3}{2}} - ln(z_{int})\right] \tag{B.16}$$

If we let $C_j = N/V$ denote the concentration of molecules of species j we can rewrite equation (B.16) as

$$\mu_j = kTlnC_j + \frac{3}{2}kTln\left(\frac{2\pi\,\hbar^2}{m_j kT}\right) + E_{int} \tag{B.17}$$

Note that E_{int} includes all internal degrees of freedom regarding vibration, rotation, electronic excitations and all the nuclear orientations.

This result for the chemical potential is the sum of the term in the logarithm of the concentration and a term that is a function only of temperature:

$$\mu_j = kTlnC_j + kT\chi_j(T) \tag{B.18}$$

where we define

$$\chi_j = \frac{3}{2} ln\left(\frac{2\pi\,\hbar^2}{m_j kT}\right) + \frac{E_{int}}{kT} \tag{B.19}$$

Note that the internal free energy E_{int} is an additive term in the chemical potential of the j^{th} chemical component.

The equilibrium condition $\sum \nu_i \mu_j = 0$ now becomes

$$\sum \nu_i \mu_j = kT \sum (\nu_i lnC_j + \nu_i \chi_j) = 0 \tag{B.20}$$

or

$$\sum lnC_j^{\nu_i} = -\sum \nu_i \chi_j \tag{B.21}$$

or

$$\prod_j C_j^{\nu_i} = e^{-\sum \nu_i \chi_j} = K_c(T) \tag{B.22}$$

Where we define the equilibrium constant $K_c(T)$ by

$$K_c(T) = e^{-\sum \nu_i \chi_j} \tag{B.23}$$

Equation (B.22) is known as the law of Mass Action.

References

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APPENDIX C

A. Diffusion

Diffusion is the random molecular transport of material to relieve a non-equilibrium condition. This transport is driven by a concentration imbalance where on the average the areas with a higher concentration of material loses or transports material to areas of lower concentrations. Additional driving forces such as electromagnet fields or perhaps gravitational fields can aid or hinder diffusion depending on their direction.

In this section the diffusion equations for positively and negatively charged particles will be derived. First we will derive the flux for a charged particle and the transport equation which determines their distribution in a solid. Then we will present solutions to the transport or diffusion equations under various conditions and assumptions.

1. Flux

Figure [1] represents the potential hills formed by the atoms of a crystal. These potential hills impede the motion of any charged particles within the crystal. The height of the potential barrier W is typically of the order of electron volts

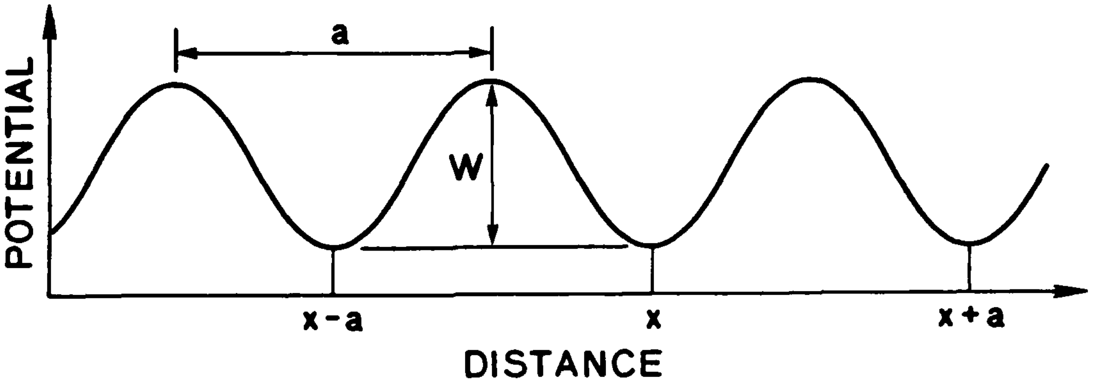

Figure C.1. Potential Distribution. Model of ionic motion within a crystal with zero electric field.

[C.1 –C.3] in most materials. The distance between successive potential barriers, a, is of the order of a lattice spacing which is several angstroms.

If a constant electric field is applied, the potential distribution as a function of distance will be tilted as shown in figure [2]. This will help positive ions move to the right and hinder their motion to the left. With the field applied the flux, J, ($J \equiv$ number of any species passing through a unit area in a unit time) at x will be the average of the fluxes at position $(x - \frac{a}{2})$ and at $(x + \frac{a}{2})$. Using the notation shown in figure [2],

$$J(x) = \frac{(J1 - J2) + (J3 - J4)}{2} \tag{C.1}$$

Consider the component J. It will be given by the product of (1) the density per unit area (normal to the direction of the flux) of particles at the potential valley at $(x - a)$, (2) the probability of jumps of any of these particles to the valley at x and (3) the frequency of attempted jumps, ν.

$$J1 = aC(x - a)e^{-\frac{q}{kT}(w - \frac{1}{2}a\mathcal{E})}\nu \tag{C.2}$$

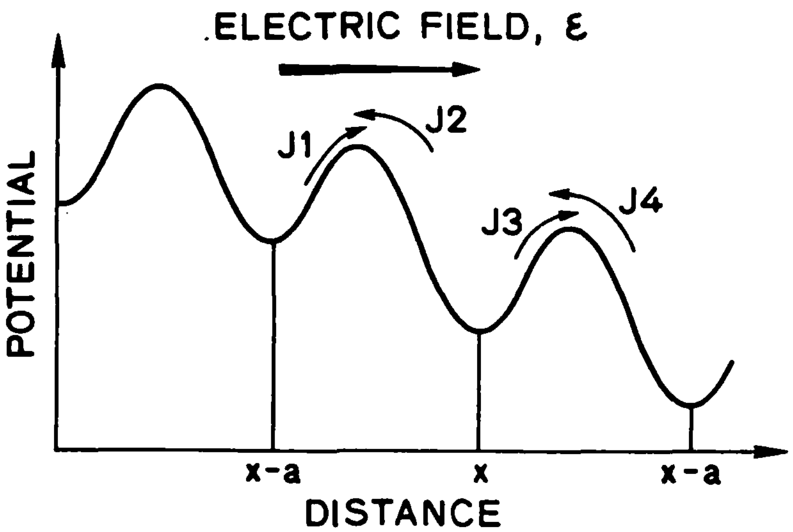

Figure C.2. Potential Distribution. Model of ionic motion within a crystal with an applied electric field.

where $aC(x-a)$ is the density per unit area of particles situated in the valley at $(x-a)$ [C.2, C.4] and the exponential factor is the probability of a successful jump from the valley at $(x-a)$ to the valley at x [C.4, C.5]. Note the lowering of the barrier due to the electric field, $\mathcal{E}$.

Likewise

$$J2 = aC(x)e^{-\frac{q}{kT}(w+\frac{1}{2}a\mathcal{E})}\nu \tag{C.3}$$

$$J3 = aC(x)e^{-\frac{q}{kT}(w-\frac{1}{2}a\mathcal{E})}\nu \tag{C.4}$$

$$J4 = aC(x+a)e^{-\frac{q}{kT}(w+\frac{1}{2}a\mathcal{E})}\nu \tag{C.5}$$

Substituting these expressions for $J1, J2, J3$, and $J4$ into equation (C.1) we get

$$J = \frac{a\nu}{2}e^{-\frac{qw}{kT}}\left[C(x-a)e^{\frac{qa\mathcal{E}}{2kT}} - C(x)e^{-\frac{qa\mathcal{E}}{2kT}} + C(x)e^{\frac{qa\mathcal{E}}{2kT}} - C(x+a)e^{-\frac{qa\mathcal{E}}{2kT}}\right] \tag{C.6}$$

making the assumption that [C.6],

$$C(x \mp a) = C(x) \mp a\frac{\partial C(x)}{\partial x} \tag{C.7}$$

J becomes

$$J = \frac{a\nu}{2}e^{-\frac{qw}{kT}}\left[C(x)\left(2e^{\frac{qa\mathcal{E}}{2kT}} - 2e^{-\frac{qa\mathcal{E}}{2kT}}\right) - a\frac{\partial C(x)}{\partial x}\left(e^{\frac{qa\mathcal{E}}{2kT}} + e^{-\frac{qa\mathcal{E}}{2kT}}\right)\right] \tag{C.8}$$

Since [C.6] $sinh\, z = \frac{e^z - e^{-z}}{2}$ and $cosh\, z = \frac{e^z + e^{-z}}{2}$,

$$J = -Dcosh\left(\frac{qa\mathcal{E}}{2kT}\right)\frac{\partial C(x)}{\partial x} + \frac{2D}{a}sinh\left(\frac{qa\mathcal{E}}{2kT}\right)C(x) \tag{C.9}$$

where $D \equiv \nu a^2 e^{-\frac{qw}{kT}}$

In the special case where $\mathcal{E} \ll \frac{2kT}{qa}$ the $cosh\, z \mapsto 1$ and the $sinh\, z \mapsto z$, [C.6], reducing J to,

$$J = -D\frac{\partial C(x)}{\partial x} + \mu\mathcal{E}C(x) \tag{C.10}$$

where $\mu \equiv (\frac{q}{kT})\nu a^2 e^{-\frac{qw}{kT}} = \frac{q}{kT}D$. By the Einstein Relationship, $\mu = \frac{q}{kT}D$, D is known as the diffusivity and μ is the mobility.

A similar derivation for the motion of a negatively charged species results in,

$$J(x) = -Dcosh\left(\frac{qa\mathcal{E}}{2kT}\right)\frac{\partial C(x)}{\partial x} - \frac{2D}{a}sinh\left(\frac{qa\mathcal{E}}{2kT}\right)C(x) \tag{C.11}$$

where $D = a^2\nu e^{-\frac{qw}{kT}} = \frac{kT}{q}\mu$.

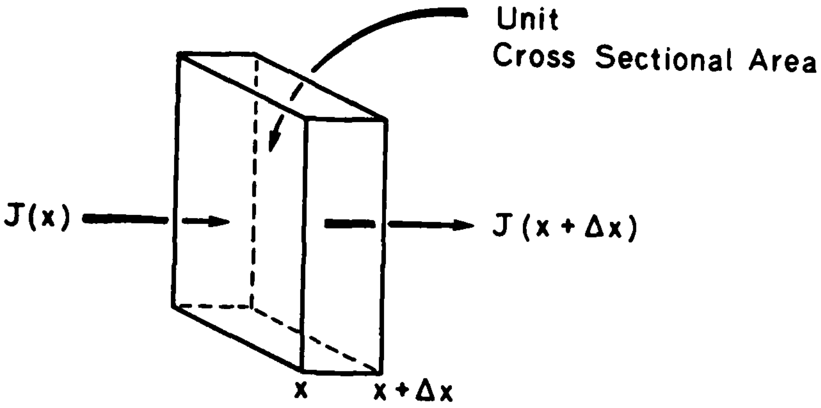

Figure C.3. Element of a Solid. No matter is created or distroyed within element.

When $\mathcal{E} \ll \frac{2kT}{qa}$ the flux for a negatively charged particles becomes,

$$J(x) = -D\frac{\partial C(x)}{\partial x} - \mu \mathcal{E} C(x) \tag{C.12}$$

2. The Transport Equation

Figure [3] shows a small element of a solid which is still large compared to atomic distances. Within this volume no material is formed or consumed. An inventory of the material contained within the element bounded by the planes at position x and $x + \Delta x$ yields

$$J_{in} - J_{out} = \frac{\textit{Increase in the density per unit area}}{\textit{unit time}} \tag{C.13}$$

In terms of concentrations, we write

$$\Delta x \frac{\partial C'}{\partial t} = J(x) - J(x + \Delta x) \tag{C.14}$$

where C' is the average concentration within the element.

When $\Delta x \mapsto 0$, $C' \mapsto C(x)$ and $\frac{J(x+\Delta x)-J(x))}{\Delta x} \mapsto \frac{\partial J(x)}{\partial x}$ we find that

$$\frac{\partial C(x)}{\partial t} = -\frac{\partial J(x)}{\partial x} \tag{C.15}$$

which is the transport equation in one dimension. If we expand our thinking to three dimensions the transport equation becomes

$$\frac{\partial C(x)}{\partial t} = -div\, J(x) \tag{C.16}$$

Combining the transport equations and our equation for flux, equation (C.10) results in

$$\frac{\partial C(x)}{\partial t} = -\frac{\partial}{\partial x}\left[-Dcosh\left(\frac{qa\mathcal{E}}{2kT}\right)\frac{\partial C(x)}{\partial x} + \frac{2D}{a}sinh\left(\frac{qa\mathcal{E}}{2kT}\right)C(x)\right] \tag{C.17}$$

If we now assume that D and $\mathcal{E}$ are independent of x and $\mathcal{E} \ll \frac{2kT}{qa}$ we may write equation (C.17), the one dimensional diffusion or transport equation, as

$$\frac{\partial C(x)}{\partial t} = D\frac{\partial C^2(x)}{\partial x^2} - \mu\mathcal{E}\frac{\partial C(x)}{\partial x} \tag{C.18}$$

Likewise for negative species under the same assumptions

$$\frac{\partial C(x)}{\partial t} = D\frac{\partial C^2(x)}{\partial x^2} + \mu\mathcal{E}\frac{\partial C(x)}{\partial x} \tag{C.19}$$

B. Solutions

Before solving the one dimensional diffusion equation let us reiterate the assumptions imposed so far and comment on their validity:

(1) Diffusion only in one dimension, normal to the surface.

(2) The electric field and the diffusion coefficient are independent of time and direction.

(3) $\mathcal{E} \ll \frac{2kT}{qa}$.

(4) Solid is homogeneous.

Assumption one is reasonable since we are considering the diffusion of charged particles and thus diffusion is enhanced parallel to the direction of the electric field. The electric field is independent of time and direction if the solid is locally uniform. The assumption that D is independent of time and direction requires a, μ and w be independent of time and direction. This is true if the solid is locally homogeneous.

To see if $\mathcal{E} \ll \frac{2kT}{qa}$ we assume $a = 10$ Å which is a conservatively high value for a lattice spacing. Then

$$\frac{2kT}{qa} = 1723.40T\, V/cm \tag{C.20}$$

where k is the Boltzmann constant and q is the charge of an electron.

Table 1 shows $\frac{2kT}{qa}$ for different values of temperature. We see that fields of $10^4 - 10^5\, V/cm$ are probably small enough to make assumption three valid.

Table C.1.

Estimates of $\mathcal{E} \ll \frac{2kT}{qa}$

Temp °K	$\frac{2kt}{qa}$
300	5.170×10^5 V/cm
600	1.034×10^6 V/cm
700	1.206×10^6 V/cm

Assumption four is valid since our samples are Czochralski grow silicon with thermally grown silicon dioxide and is therefore homogeneous, at least locally.

Using these assumption we solve the diffusion equation in one dimension for positive particles, equation (C.18), for the following boundary conditions.

(1) $C(0,t) = C_s$.

(2) $C(\infty,t) = 0$.

(3) $C(x,0) = 0$.

where C_s is the solid solubility of the particle in the silicon dioxide. The solution can be shown to be [C.7–C.9].

$$C(x) = \frac{C_s}{2}\left[erfc\left(\frac{x - \frac{qD\mathcal{E}t}{kT}}{2(Dt)^{\frac{1}{2}}}\right) + e^{\frac{q\mathcal{E}x}{kT}} erfc\left(\frac{x + \frac{qD\mathcal{E}t}{kT}}{2(Dt)^{\frac{1}{2}}}\right)\right] \tag{C.21}$$

Figure [4] is a plot of this equation for 300°C, 1.5 hours, $\mathcal{E} = 5.2 \times 10^4 V/cm$ and a solid solubility of, C_s, of $3 \times 10^{18} cm^{-3}$. Different diffusivities are shown in the figure to allow a comparison with the silver data presented eatlier. This solution to the diffusion equation models reality when the substance the particles are diffusing through is semi-infinite. As a further example figure [5] is a plot of equation (C.21) when $T = 100°C$, $t =$ one year, $\mathcal{E} = 10^6 V/cm$, $C_s = 3 \times 10^{18} cm^{-3}$, and the diffusivity takes on the values shown in the figure.

As an approximation to the case when the diffusing particles pile up at the SiO_2/Si interface, equation (C.18) may be solved with following boundary conditions.

(1) $C(0,t) = C_s$.

(2) $C(x,0) = 0$.

(3) $\frac{\partial C(a,t)}{\partial x} = 0$

where a is the film thickness.

The solution to these conditions is [C.7 – C.9],

$$C(x,t) = C_s\left[1 - 2\sum_{n=1}^{\infty}\frac{\left(\beta_n^2 - \left(\frac{q\mathcal{E}}{2kT}\right)^2\right)^{\frac{1}{2}}}{a\beta_n^2 + \frac{q\mathcal{E}}{2kT}}e^{-\beta_n^2 Dt}e^{\frac{q\mathcal{E}}{2kT}}sin\left(\left(\beta_n^2 - \left(\frac{q\mathcal{E}}{2kT}\right)^2\right)^{\frac{1}{2}}x\right)\right] \tag{C.22}$$

where the β_n's are the positive roots of

$$tan\left(\left(\beta^2 - \left(\frac{q\mathcal{E}}{2kT}\right)^2\right)^{\frac{1}{2}}a\right) = -\frac{2kT}{q\mathcal{E}}\left(\beta^2 - \left(\frac{q\mathcal{E}}{2kT}\right)^2\right)^{\frac{1}{2}} \tag{C.23}$$

Figure [6] is a plot of this equation for 300°C, 1.5 hours, $\mathcal{E} = 5.2\times 10^4 V/cm$, $C_s = 3\times 10^{18} cm^{-3}$, and a films thickness of 5700Å. Figure [7] is a plot of equation (C.22) with T= 100°C, $\mathcal{E} = 10^6 V/cm$, $C_s = 3\times 10^{18} cm^{-3}$, $a = 5700$ Å, and a time of one year.

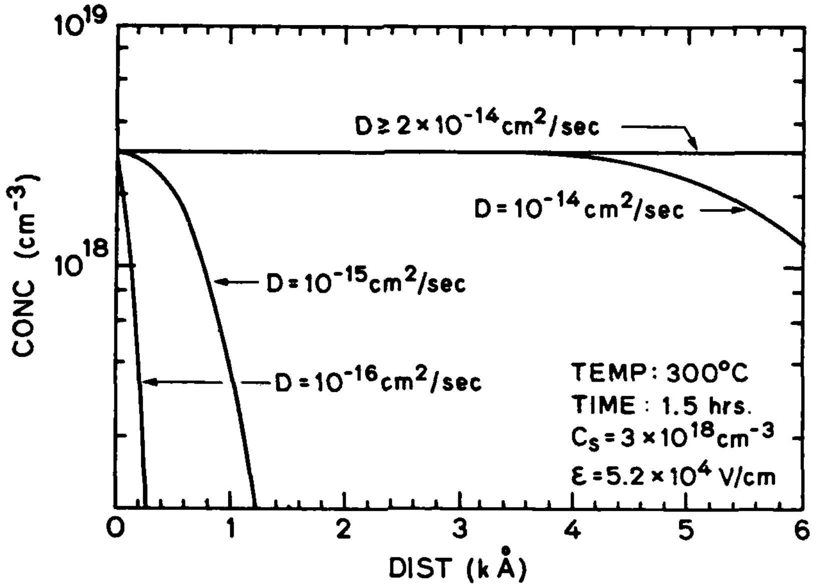

Figure C.4. Solution to the Diffusion Equation for a Semi- infinite Slab. $300°C$, 1.5 hours, $\mathcal{E} = 5.2 \times 10^4 V/cm$ and $C_s = 3 \times 10^{18} cm^{-3}$.

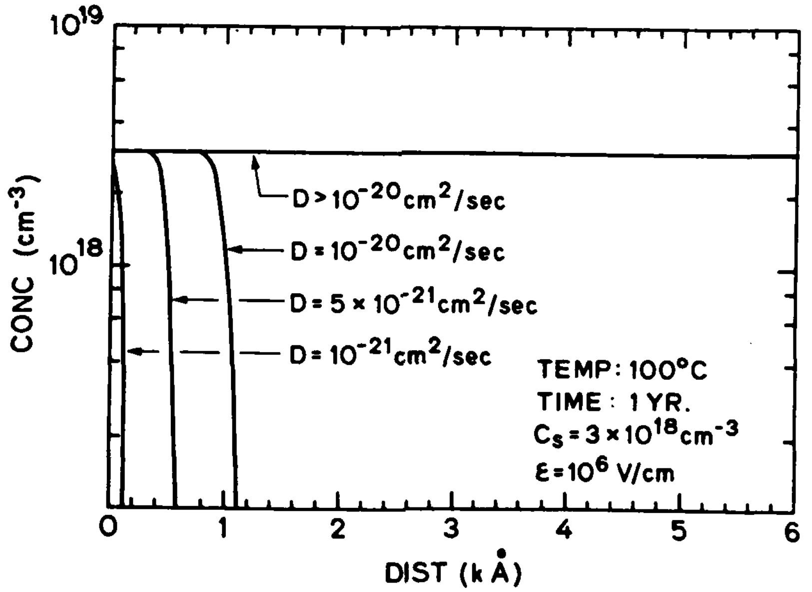

Figure C.5. Solution to the Diffusion Equation for a Semi- infinite Slab. $100°C$, $t =$ one year , $\mathcal{E} = 10^6 V/cm$ and $C_s = 3 \times 10^{18} cm^{-3}$.

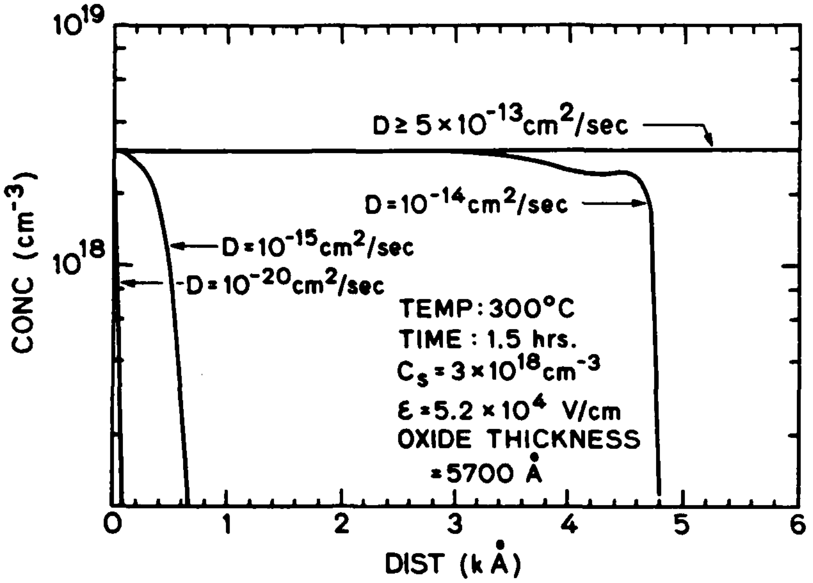

Figure C.6. Solution to the Diffusion Equation for a given film thickness. $300°C$, 1.5 hours, $\mathcal{E} = 5.2 \times 10^4 V/cm$, $C_s = 3 \times 10^{18} cm^{-3}$ and a film thickness of 5700 Å.

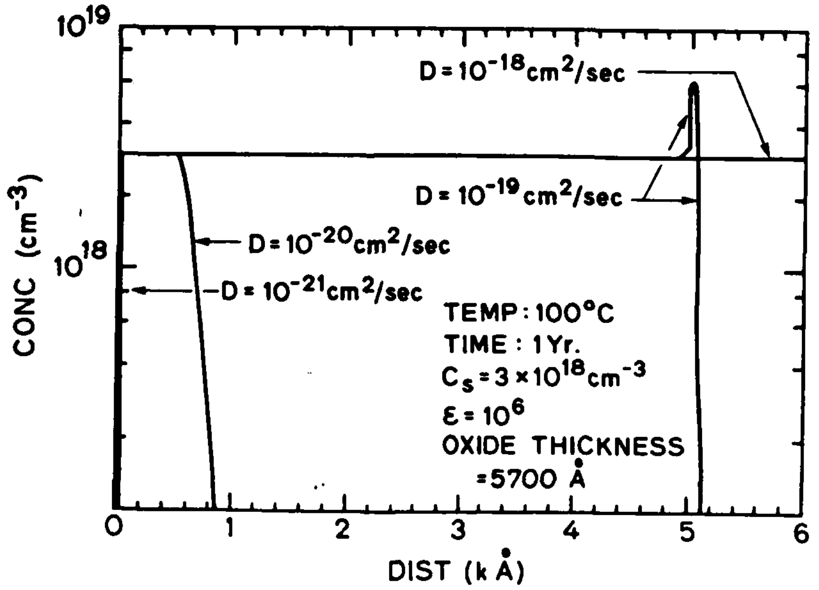

Figure C.7. Solution to the Diffusion Equation for a given film thickness. $100°C$, t = one year , $\mathcal{E} = 10^6 V/cm$, $C_s = 3 \times 10^{18} cm^{-3}$ and a film thickness of 5700 Å.

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