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Gettering of transition metals by cavities in silicon formed by helium ion implantation

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Abstract

We have recently completed studies which quantitatively characterize the ability of nanometer-size cavities formed by He ion implantation to getter detrimental metal impurities in Si. Cavity microstructures formed in Si by ion implantation of He and subsequent annealing have been found to capture metal impurities by two mechanisms: 1) chemisorption on internal walls at low concentrations and 2) silicide precipitation at concentrations exceeding the solid solubility. Experiments utilizing ion-beam analysis, cross-sectional transmission electron microscopy, and secondary ion mass spectrometry were performed to quantitatively characterize the gettering effects and to determine the free energies associated with the chemisorbed metal atoms as a function of temperature. Mathematical models utilizing these results have been developed to predict gettering behavior.

1. Introduction

Transition-metal impurities degrade Si-based microelectronics by introducing deep electronic levels into the Si band gap and by precipitating in critical regions, such as Si-SiO_2 interfaces, leading to electrical breakdown.[1] These effects are enhanced by the rapid interstitial diffusion of transition metals in Si which allows growing precipitates to draw metal atoms from a macroscopic wafer volume during processing [2,3]. Projected specifications for future Si devices give a maximum metal impurity content of $2.5\text{x}10^9$ atoms/cm^2 by the year 2007 [4]. In device processing, Si manufacturers often supplement stringent clean-room procedures with gettering, a process in which metal impurities are captured by impurity sinks located in a sacrificial portion of the wafer. These sinks are usually produced by introducing imperfections into the Si lattice such as SiO_2 precipitates and lattice defects, which nucleate silicide precipitation [1]. Ion implantation has been one of the methods explored for the introduction of gettering centers for more than 20 years [5].

We have investigated the ability of cavity microstructures formed by He ion implantation and annealing to act as gettering centers [6-9]. The results presented here expand on earlier work by

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quantitatively characterizing the trapping of several transition metals (Cu, Au, Co, and Fe) at the internal surfaces of the cavities. Evidence indicates that the observed binding arises from at least two mechanisms: one is chemisorption on the cavity walls up to approximately one monolayer (ML), and the other is formation of three dimensional metal-silicide precipitates within the voids [10]. The reactions involving second-phase precipitation reduce the solution concentration to a characteristic solid solubility and no further. The chemisorption reaction is important because it supersedes silicide precipitation when the impurity solution concentration is less than its solid solubility. Therefore, lower impurity level concentrations can be obtained, and silicide particles that have formed at unwanted locations, such as the base of gate oxides, can be dissolved, making cavity trapping an attractive alternative for gettering. Quantitative information on the binding energies of Cu, Au, Co, and Fe to cavity walls relative to solution and relative to the silicide phase as a function of temperature has been obtained. Also, mathematical models using these results have been developed to predict gettering behavior in Si for both conventional internal gettering at SiO_2 precipitates and gettering by a cavity layer as a function of time and temperature.

2. Method

The cavities of this study were formed by ion-implanting He into float-zone (111) Si to a concentration of several atomic percent and then annealing at a temperature of 700°C or higher. Earlier studies have shown that this produces a layer of faceted voids with diameters $\geq$ 10nm from which the He has diffused and extensive removal of the ion implanted damage [7,11,12]. The resulting internal surfaces typically have a combined area of several times the sample area and are strongly reactive [11]. A representative cavity microstructure and corresponding depth profile of Cu gettered to the cavity layer from a remotely located silicide are shown in Figs. 1a and 1b, respectively.

In this study, two types of experiments were performed in order to determine the relative binding strengths of the metal atoms (Cu, Au, Co, and Fe) to the cavity walls. In one type a high dose of metal atoms was implanted into Si in order to form a metal silicide. A single cavity layer was located at a different depth than the silicide. When these samples were annealed, the silicide acted as an inexhaustible source of metal atoms to solution from which the cavities would getter the metal atoms. The second type of experiment consisted of Si samples with two cavity layers located at different depths. In these samples a lower dose of metal atoms was implanted so that cavity wall saturation would not occur [11]. When these samples were annealed, the redistribution of the metal atoms among the initial implanted layer and the two cavity layers could be studied. Rutherford backscattering spectrometry (RBS) and secondary ion mass spectrometry (SIMS) were used to measure the metal atom redistributions. The results of these experiments were then analyzed to obtain the binding strengths of the cavity sinks, as discussed in the following.

In order to quantify the binding of the metal atoms by chemisorption and silicide precipitation we must first outline the formalism used. The strengths of these reactions are expressed in terms of a Gibb's free energy change associated with the transfer of one metal atom from the bound state to interstitial solution, or, in the context of this paper, the binding free energy,

$$\Delta G \equiv \Delta H - T\Delta S_{ex}. \tag{1}$$

Here ΔH is the change in enthalpy and ΔS_{ex} is the residual change in entropy after the configurational contributions due to fractional occupation of multiple solution and cavity-wall sites are taken into account separately. The solution concentration of metal atoms in equilibrium with cavity-wall chemisorption is then given by,

$$C_s[cav] = \{\theta/(1-\theta)\}\exp(-\Delta G_{cav}/kT) \tag{2}$$

where C_s is expessed as atomic fraction and θ is the fractional occupancy of the trap sites. Eq. (2) assumes that metal atoms on different sites do not interact with each other, a simplifying approximation whose accuracy increases with increasing temperature and decreasing occupancy. The corresponding equation for equilibrium between solution and precipitated metal-silicide phase is

$$C_s[sil] = \exp(-\Delta G_{sil}/kT). \tag{3}$$

Eqs. (1-3) describe thermodynamic equilibrium. They are also the basis for source terms in the diffusion equation when the thermal evolution toward an equilibrium system is modeled, as detailed elsewhere [7]. The objective is then to evaluate ΔG_{cav} for the gettering temperatures.

When $\theta << 1$ for cavities in equilibrium with the silicide phase, the gettering energetics can be ascertained by combining Eqs. (2) and (3) by using the equilibrium condition $C_s[cav] = C_s[sil]$ to obtain

$$\theta/(1-\theta) = \exp\{(\Delta G_{cav}-\Delta G_{sil})/kT\}. \tag{4}$$

By experimentally measuring the amount of gettered metal in a cavity layer supplied by a remotely located silicide source, i.e. determining θ, and taking ΔG_{sil} from the literature [2], ΔG_{cav} is readily obtained from Eq. (4).

As the equilibrium value of θ approaches 1, however, Eq. (4) no longer serves to determine ΔG_{cav}, and a different technique must be applied. In this case, Rutherford backscattering spectrometry is used to observe the diffusive redistribution of metal atoms from one cavity layer to another. One cavity layer contained chemisorbed metal atoms at zero time while the other was initially unoccupied. The θ dependence in Eq. (2) gives rise to a difference in solution concentration, ΔC_s, from one layer to another when $\theta_1 \neq \theta_2$, causing an interlayer diffusion flux, Φ, which in the limit of steady-state diffusion is given by

$$\Phi \cong \Delta C_s D N_{Si} / \Delta x \qquad (5)$$

where D is the metal diffusion coefficient as obtained from the literature [2], N_{si} is the atomic density of Si, and Δx is the average interlayer diffusion distance. From Eq. (2) we can define the difference in the solution concentration in equilibrium with silicide by

$$\Delta C_s \approx [\theta_1/(1-\theta_1) - \theta_2/(1-\theta_2)]\exp(-\Delta G_{cav}/kT). \qquad (6)$$

Using the experimentaly measured flux, Φ, ΔG_{cav} can then be extracted from Eq. (5). Similarly, this procedure can be used to obtain ΔG_{sil}, where the measured flux is from a silicide containing layer to a cavity layer, then Eq. (5) is again applicable. When the cavity sinks bind substantially more than the silicide, one has $\Delta C_s \approx C_s[sil] = \exp(-\Delta G_{sil}/kT)$. This procedure was used to determine ΔG_{sil} for the Cu and Au, where previous information is less precise than for Co and Fe.

3. Results and Discussion

Two types of cavity-gettering behavior have been observed in the studies of Cu, Au, Co, and Fe impurities in equilibrium with the metal-silicide phase. The first type, as displayed by Cu and Au, is where the cavitiy walls become saturated with metal atoms at about one monolayer of coverage, or $\theta \approx 1$ [7,8]. This implies that $\Delta G_{cav} \gtrsim \Delta G_{sil}$ for these metals. The saturation of Cu on the cavity walls is demonstrated in Fig. 1(b). The second type, as in the cases for Co and Fe, is where the cavities are far from saturation ($\theta <$ 0.01 ML [9,13]), or $\theta << 1$, which signifies that $\Delta G_{cav} < \Delta G_{sil}$. In both cases the source of metal atoms was an excess of the equilibrium metal-silicide phase, formed at a different depth by implantaion and annealing prior to the introduction of the cavities. This procedure stabilized the solution concentration at the solubility during subsequent anneals preventing supersaturation, thereby avoiding gettering due to silicide formation in the cavities and leaving only the wall-chemisorption reaction of interest.

For the case of Co and Fe, where $\theta << 1$, we obtained $\Delta G_{cav}[Co]$ and $\Delta G_{cav}[Fe]$ by experimentally determining θ for the cavities in equilibrium with excess metal silicide, took $\Delta G_{sil}[Co] = 2.83$ eV - 7.6 kT and $\Delta G_{sil}[Fe] = 2.94$ eV - 8.2 kT from the literature [2], and substituted the results into Eq. (4). The fractional wall occupancy, θ, was defined by the measured areal density of gettered Co and divided by the number of cavity wall surface sites as estimated by TEM [11].

For the case of Cu and Au, where $\theta \approx 1$, we must make use of the analysis of the layer to layer redistribution of metal atoms, as discussed in Sect. 2. The interlayer redistributions are illustrated by the results for Au in Fig. 2. The areal density of metal atoms in the initially unoccupied cavity layer is plotted versus anneal time. Fig. 2(a) shows the redistribution from a silicide layer to a cavity layer, and Fig. 2(b) shows the redistribution between two cavity layers. Note that the transfer from silicide to cavity sinks exhibits an abrupt saturation level corresponding within experimental uncertainty to 1 ML on the cavity walls, with a small temperature dependence ascribed to changes in cavity microstructure. No comparable discontinuity is seen for the redistribution between two cavity layers, where the θ-dependent chemical potentials in the two layers are expected to approach one another in a continuous fashion. Also, as the anneal temperature decreases, the asymptotic fraction of metal atoms transferred is progressively less than the approximately 50% expected from the above arguments based on Eqs. (2) and (4). This is apparent in Fig. 2(b) where 50% of the implanted Au dose is 7.5×10^{15} atoms/cm^2. The departure from 50% disappeared when the initial implant dose of the Au was reduced by a factor of five, leading us to hyupothesize that the cause was ordered islands of chemisorbed Au co-existing with random-site chemisorption on the cavity walls.[8] This tends to occur for values of θ above a temperature-dependent threshold, and the onset of the two-phase surface condition halts the θ dependence of Eq. (2) which gives rise to the interlayer redistribution. No such effect was evident in our studies of Cu.

The theoretical curves in Fig. 2 were calculated using a numerical solution of the diffusion equation with source terms based on Eqs. (2) and (3) as described elsewhere [7] rather than employing the tutorial simplifications of Eq. (4). For the case of the gold, the treatment was extended to account for the effect of ordered-island chemisorption [8], with adjustable binding free energies being included for both the ordered and random chemisorption states. The resulting fits provide a good and internally consistent description of all of the experimental data.

The binding free energies for cavity-wall chemisorption and silicide precipitation of Cu, Au, Co, and Fe are plotted versus temperature in Fig. 3. (In the case of Au chemisorption, the values are for ordered islands co-existing with random-site chemisorption, which are slightly higher than those of random-site chemisorption alone.) These results allow the prediction of gettering behavior. Two trends are readily apparent in Fig. 3, and both can be understood qualitatively on physical grounds. First, as stated previously, $\Delta G_{cav} > \Delta G_{sil}$ for Cu and Au, whereas $\Delta G_{cav} < \Delta G_{sil}$ for Co and Fe. Monovalent metals optimize their bonding by reacting with the single dangling orbitals of Si surface atoms, whereas the higher valences of Co and Fe drive these species to precipitate as three-dimensional phases where the metal atom can bond to a larger number of Si atoms. Second, there is predominantly an upward trend in binding free energy with decreasing temperature, consistent with a positive $T\Delta S_{ex}$. We believe that this represents a relatively large vibrational entropy of metal atoms in the tetrahedral interstitial solution site where there is substantial open volume and the metal atoms are not strongly bonded into the host lattice. The exceptions to this trend are the Cu chemisorption where the range of data is too limited to establish a temperature dependence, and for the precipitated Si-Au phase, which is actually molten at the anneal temperature (850°C) and is therefore expected to have a relatively high entropy.

4. Theoretical prediction of gettering ability

Using the binding free energies shown in Fig. 3, a theoretical prediction of the performance of different gettering mechanisms can be demonstrated. Figs. 4(a) and 4(b) illustrate the ability of cavities to reduce the impurity concentration in solution 1 μm below the surface at various temperatures for Cu and Fe impurities, respectively. The model allowed for both chemisorption on cavity walls and silicide precipitation in the cavities to occur concurrently. Included for comparison are model predictions for conventional internal gettering, where SiO_2 particles and related defects within the underlying bulk of Czochralski wafers provide sites for nuleation and growth of silicide precipitates. The parameterization of this latter process uses a product of sink density and sink radius of $4.8 \times 10^{15} cm^{-2}$ [14]. The plots show impurity concentration versus anneal time, where the initial impurity concentration was 10^{12} atoms/cm^3, typical of hiqh quality wafers, uniformly distributed throughout the sample. For the cavity case, the 1 μm thick cavity layer was positioned 5 μm below the surface, whereas the SiO_2 precipitate case consisted of a 10 μm near-surface sink-free zone with the precipitates spread evenly throughout the rest of a 0.5 mm thick Si wafer.

In the cases where only internal gettering by silicide precipitation is present (dashed lines) for both Cu and Fe, it is evident that the gettering occurs, however, it only occurs when the solid solubility at the anneal temperature is below the initial impurity solution concentration, i.e. below 500°C for Cu and below 800°C for Fe. When the SiO_2 precipitates do getter, they can only pull the solution concentration down to the solid solubility and no further.

For both the Cu and Fe impurity cases with cavities (solid lines) there are three distinct regions. In the first region the initial impurity concentration drops very rapidly to some lower solution concentration. This can be explained by the proximity and large capture cross-section of the cavities. The second or middle region shows what happens as the metal atoms continue to diffuse to the cavities from the bulk of the wafer. The third region shows the solution concentration in equilibrium after long times. The slope of the second region is dependent upon the time it takes the metal atoms to diffuse from the bulk of the sample to the cavity layer. At higher temperatures, a pronounced minimum is detected as a function of time. This is explained by two opposing trends: the diffusion limited transfer of metal atoms from 1 μm to the nearby sinks at short times, and the increase in $C_s[cav]$ at longer times as the slower acquisition of metal atoms from the underlying bulk increases θ (see Eq. (2)). At lower temperatures, the metal atoms diffuse more slowly to the cavity sinks from the bulk of the sample. Once the metal atoms have completely diffused to the cavity traps, the solution concentration drops quickly to the equilibrium concentration.

It is easily seen that for the case of the Cu impurities, the relatively strong cavity traps getter much better, > 4 orders of magnitude, at all temperatures compared to the weaker silicide precipitation. Similarly for the Fe, for initially low impurity concentrations, the cavity sinks tend to pull the Fe solution concentration down by 1-2 orders of magnitude lower at relatively short times, and slightly lower than the solid solubilities at long times, except for the 400°C case where both gettering mechanisms pull the solution concentration down to the solid solubility at equilibrium. However, in all cases, the solution concentration in the near-surface region is reduced faster by the cavitiy sinks by about an order of magnitude in time.

5. Conclusions

We have quantified the ability of cavities formed in Si by He ion implantation and annealing to getter the transition metals Cu, Au, Co, and Fe. An analysis of the redistribution of metal atoms during the gettering process allows for the determination of the free binding energy relative to solution. For Cu and Au, $\Delta G_{cav} > \Delta G_{sil}$, whereas for Co and Fe the opposite is true, $\Delta G_{cav} < \Delta G_{sil}$. A theoretical model was used to predict the gettering behavior of two gettering mechanisms. By applying this model to cavity traps and internal gettering at SiO_2 precipitates, the gettering effectiveness was determined for various temperatures and initial impurity concentrations. For Cu and Au, the cavities strongly outperformed the internal gettering sites over the range of temperatures studied. Although the binding free energies for Co and Fe are not as large as those of their respective silicides, when initial impurity concentrations are below the threshold for silicide precipitation, substantial gettering can occur. The results indicated that cavities can induce reductions in the impurity solution concentrations by several orders of magnitude, even for the least favorable case of Fe. Cavity sinks offer the feasability of gettering on the device side as well as the back side of wafers. Therefore, the ability of cavity gettering to attain very low level impurity content in Si wafers is a potential application that appears technologically attractive in the near future.

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Figure Captions

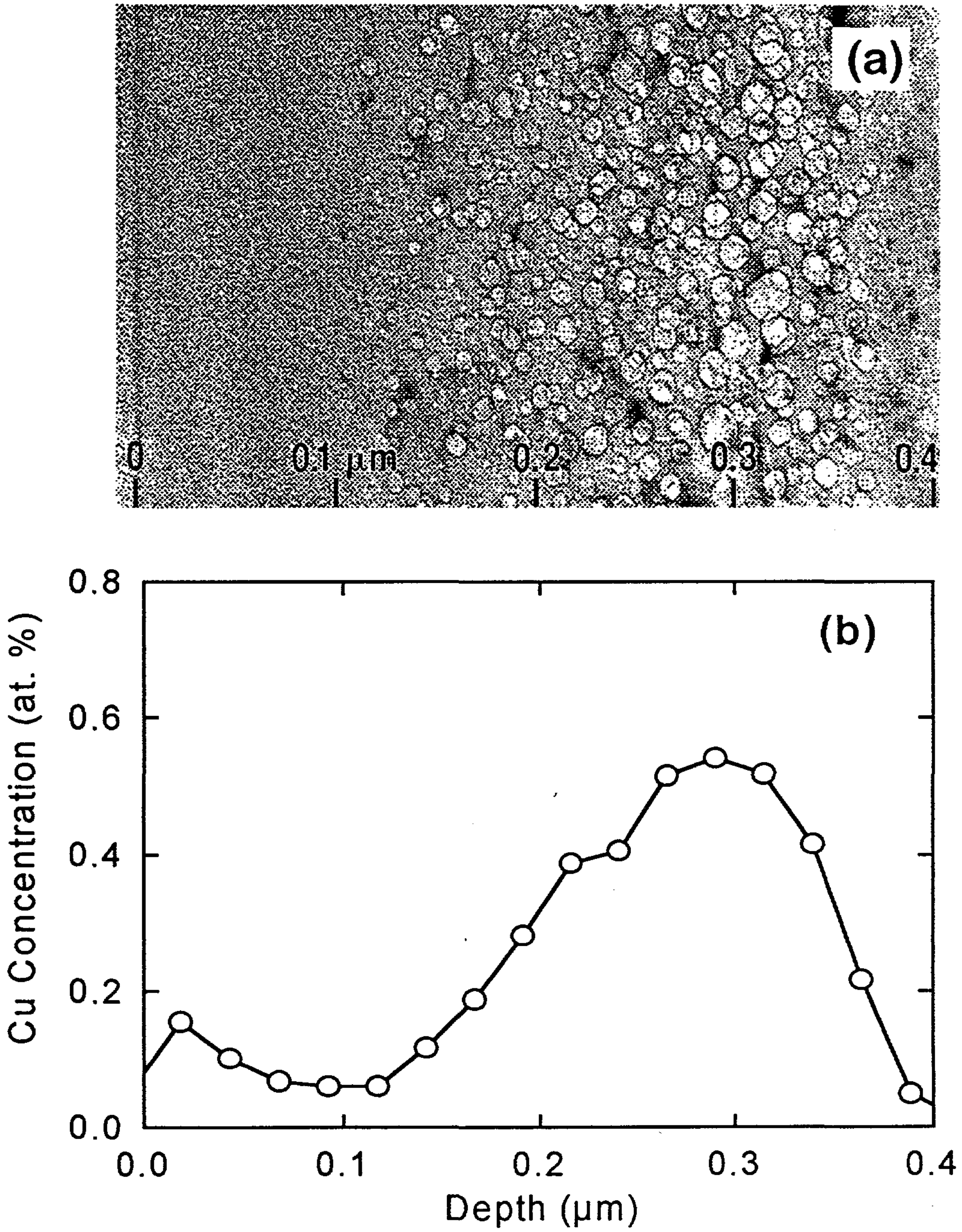
1. (a) Cross-Section TEM image of cavities in (100)-Si implanted with 10^{17} He/cm^2 at 30 keV and then vacuum annealed at 700°C for 0.5 h. (b) Depth profile of Cu in a cavity layer similar to (a) obtained by RBS. The cavity walls are saturated with $5\text{x}10^{15}$ Cu/cm^2, corresponding to about one monolayer on the cavity surface.

2. Diffusive redistribution of Au for (a) silicide-to-cavity and (b) cavity-to-cavity layers. The silicide-to-cavity sample was implanted with 10^{16} Au/cm^2 at 300 keV, annealed at 850°C to form silicide, then implanted with 10^{17} He/cm^2 at 150 keV on the same side and annealed for 50 h at 750°C to form cavities and induce gettering. For the cavity-to-cavity redistribution the two cavity layers were formed prior to Au implantation by implanting 10^{17} He/cm^2 at 30 and 180 keV and annealing at 900°C for 1 h. The Au was subsequently implanted on the same side with $1.5\text{x}10^{15}$ Au/cm^2 at 300 keV. After anealing the measurements were carried out by RBS.

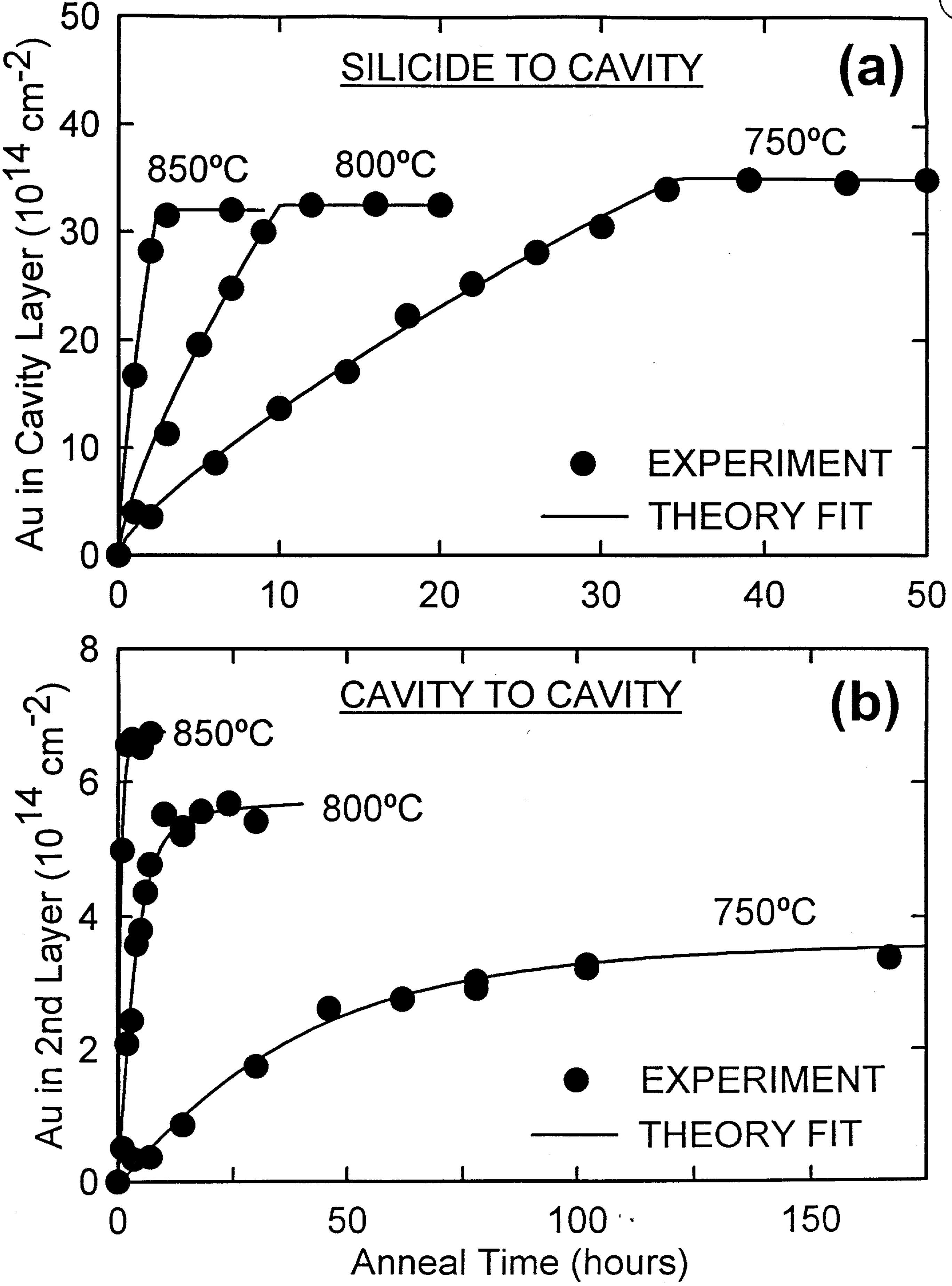
3. Binding free energies relative to solution of transition metals for both chemisorption on cavity walls and precipitation of equilibrium silicide phases.

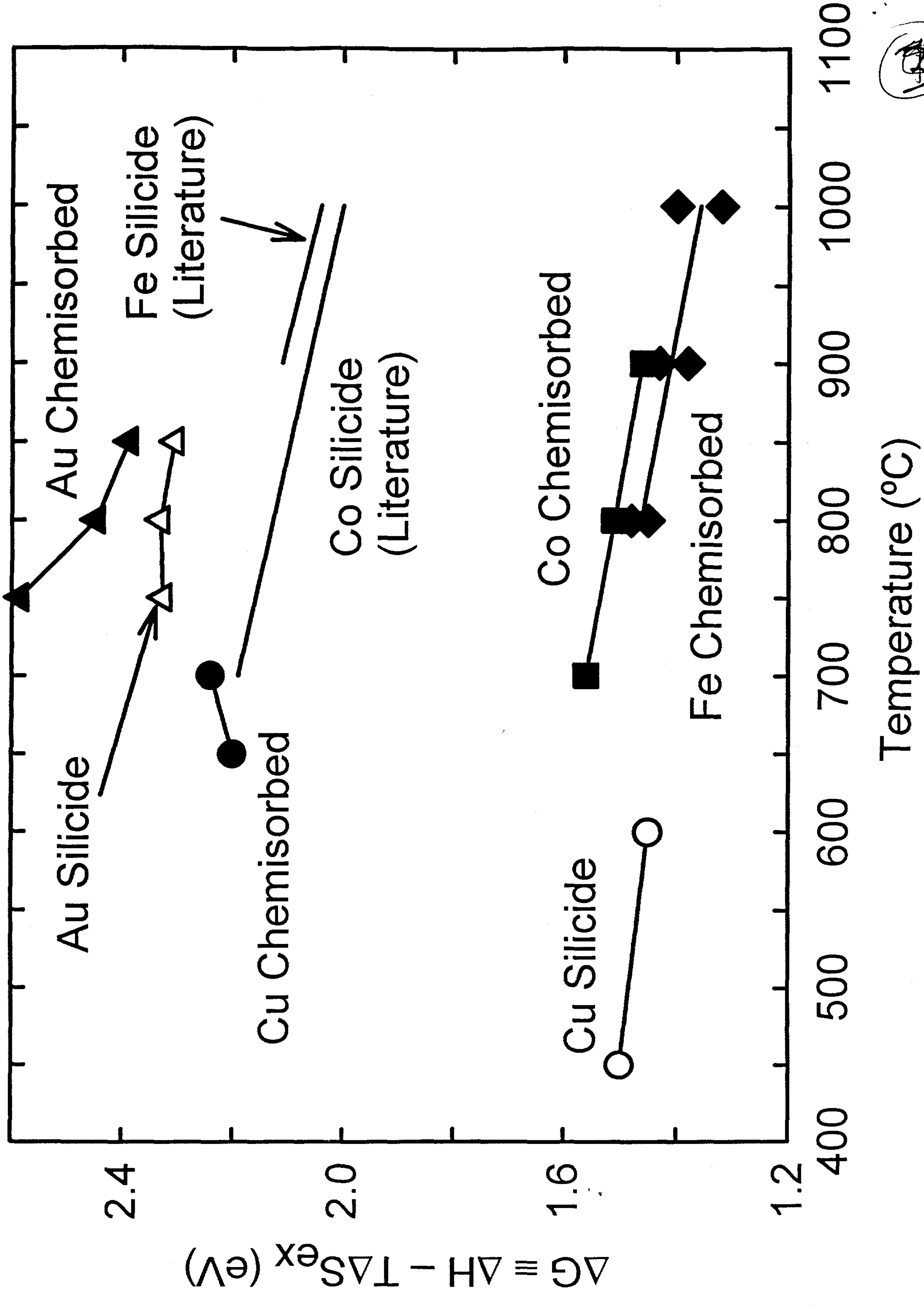
4. Theoretical model yielding a prediction of gettering in Si of (a) Cu and (b) Fe by cavities and SiO_2 precipitates for anneal temperatures of 400 to 1000°C. The plots show the impurity solution concentration at a depth of 1 μm from the surface, with initial impurity concentrations of 10^{12} atoms/cm^3 for all cases.

①

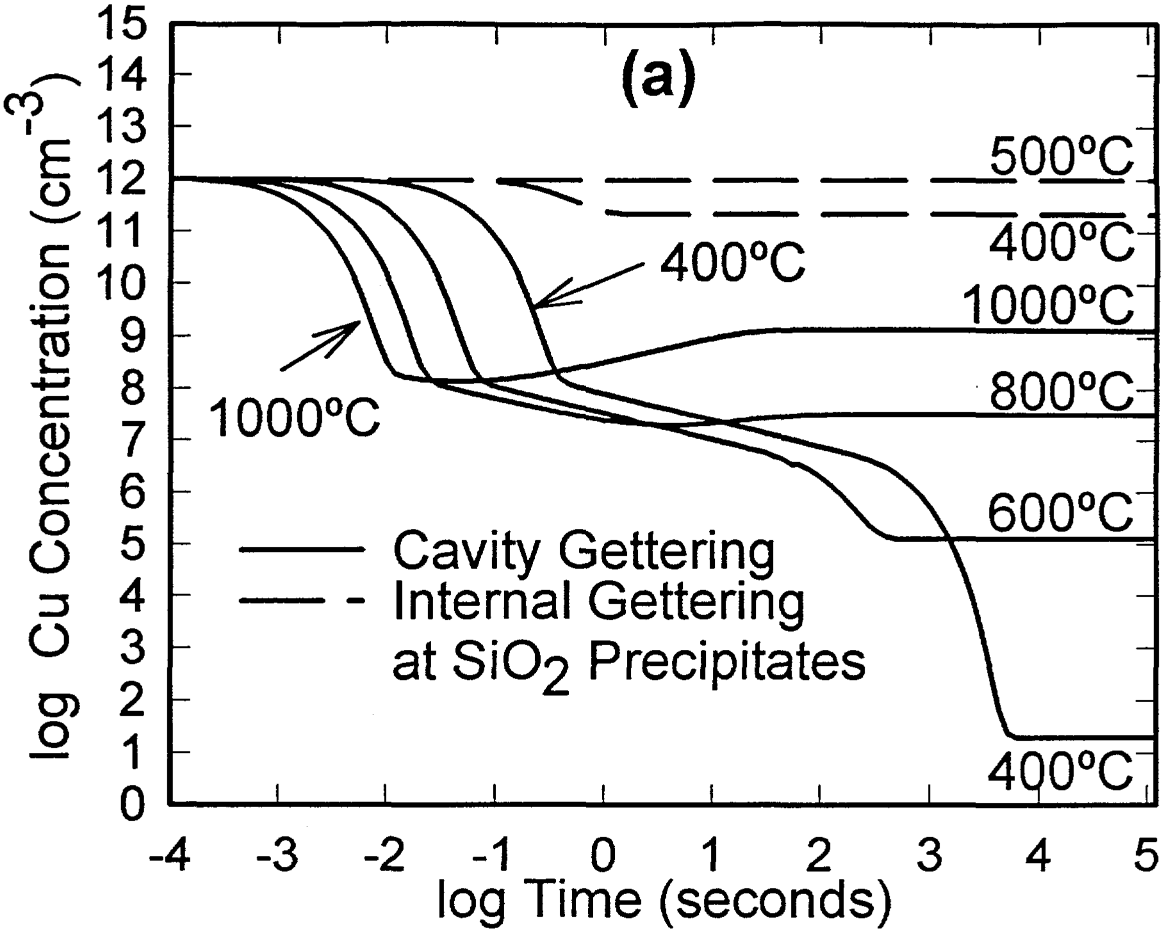

(a)
0
0.1 µm
0.2
0.3
0.4
(b)
Cu Concentration (at. %)
0.0
0.2
0.4
0.6
0.8
Depth (µm)
0.0
0.1
0.2
0.3
0.4

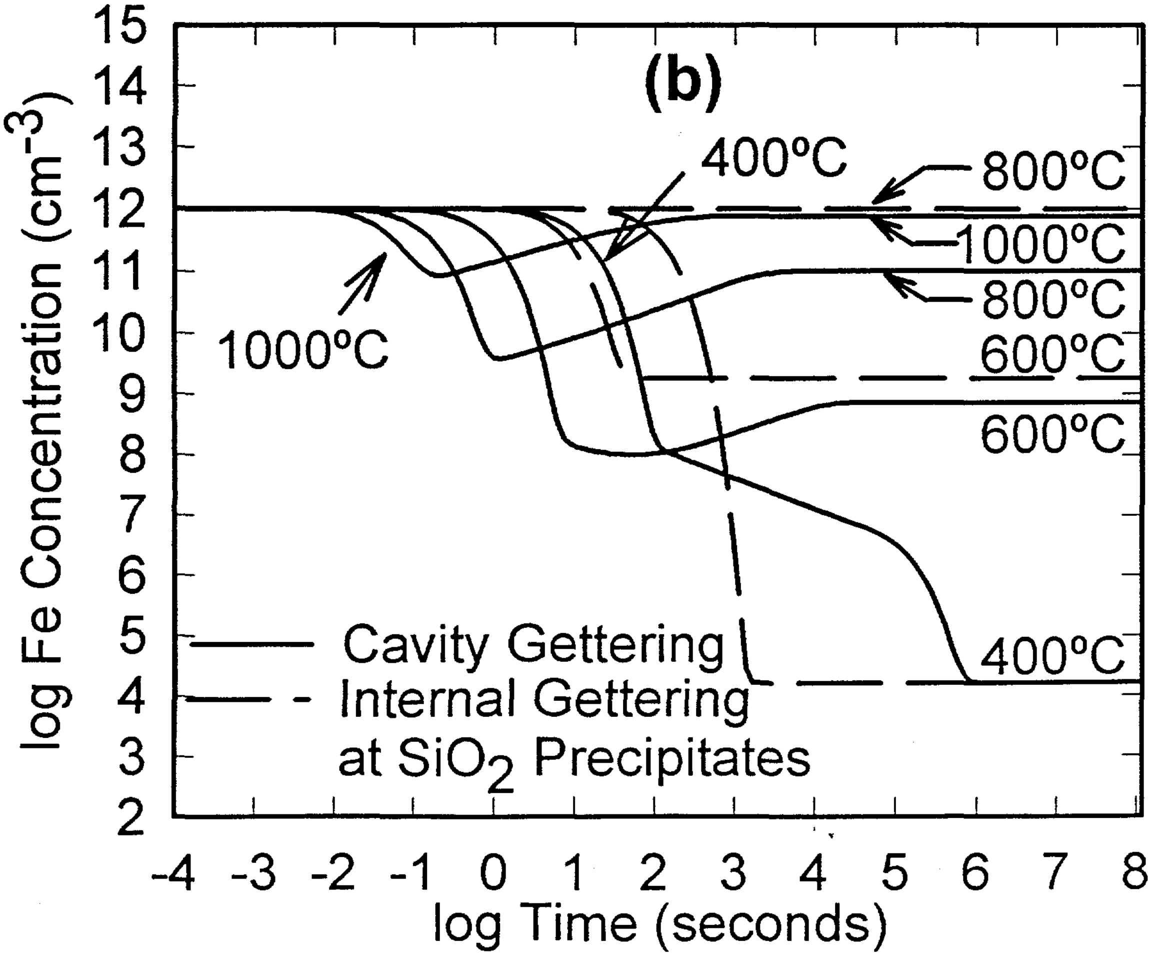
③


SILICIDE TO CAVITY
(a)
Au in Cavity Layer (10^{14} cm^{-2})
0
10
20
30
40
50
850°C
800°C
750°C
● EXPERIMENT
THEORY FIT
0
10
20
30
40
50
CAVITY TO CAVITY
(b)
Au in 2nd Layer (10^{14} cm^{-2})
0
2
4
6
8
850°C
800°C
750°C
● EXPERIMENT
THEORY FIT
0
50
100
150
Anneal Time (hours)


ΔG ≡ ΔH − TΔS_ex (eV)
2.4
2.0
1.6
1.2
Temperature (°C)
400
500
600
700
800
900
1000
1100
Au Chemisorbed
Au Silicide
Fe Silicide (Literature)
Co Silicide (Literature)
Cu Chemisorbed
Cu Silicide
Co Chemisorbed
Fe Chemisorbed

4


(a)
log Cu Concentration (cm^{-3})
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
500°C
400°C
400°C
1000°C
1000°C
800°C
600°C
400°C
Cavity Gettering
Internal Gettering
at SiO_2 Precipitates
-4
-3
-2
-1
0
1
2
3
4
5
log Time (seconds)


(b)
log Fe Concentration (cm^{-3})
15
14
13
12
11
10
9
8
7
6
5
4
3
2
400°C
800°C
1000°C
1000°C
800°C
600°C
600°C
400°C
Cavity Gettering
Internal Gettering
at SiO_2 Precipitates
-4
-3
-2
-1
0
1
2
3
4
5
6
7
8
log Time (seconds)