Strong segregation gettering of transition metals

by implantation-formed cavities and boron-silicide precipitates in silicon

S.M. Myers, G.A. Petersen, D.M. Follstaedt, T.J. Headley, J.R. Michael, and C.H. Seager

Sandia National Laboratories, P.O. Box 5800, Albuquerque, New Mexico 87185-1056 USA

Abstract

We have mechanistically and quantitatively characterized the binding of transition-metal impurities in Si to cavities formed by He implantation and to B-Si precipitates resulting from B implantation. Both sinks are inferred to act by the segregation of metal atoms to pre-existing low-energy sites, namely surface chemisorption sites in the case of cavities and bulk solution sites in the case of the B-Si phase. These gettering processes exhibit large binding energies, and they are predicted to remain active for arbitrarily small initial impurity concentrations as a result of the segregation mechanisms. Both appear promising for gettering in Si devices.

1. Introduction

The removal of detrimental transition-metal impurities from the device region of Si wafers by gettering at remotely located sinks is a widely used and successful supplement to stringent clean-room procedures [1,2]. Currently, most gettering is based upon the introduction into the Si lattice of imperfections, such as extended defects and SiO₂ precipitates, which serve as nucleation centers for precipitation of the silicide phases of the metal impurities. While effective, this approach has the inherent limitation that the solution concentration of a metal impurity can be reduced to the thermodynamic solid solubility and no further. Since the solubilities exceed acceptable impurity levels at the elevated temperatures of device processing, provisions must be made for subsequent gettering at lower temperatures. Moreover, the impact of this constraint will increase with the continuing reduction of metal-impurity tolerances [3]. A further important point is that gettering by silicide precipitation cannot directly dissolve the silicide particles that form at such critical locations as the base of gate oxides because the metal chemical potential is the same at the particles and sinks.

The above considerations point to a need for gettering methods that remain effective at

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concentrations below the metal solubility and provide useful gettering at the high temperatures of device processing. A process of this type that has received wide attention is phosphorus-diffusion gettering, where P is diffused into the back of the wafer from a layer of phosphosilicate glass [2]. The underlying mechanisms may include P-related enhancement of metal solubilities and localized kinetic enrichment of the metal concentration due to interstitial-defect flows associated with P diffusion. While P-diffusion gettering is known to be effective, available information does not allow quantitative prediction of the reductions in impurity concentrations. Gettering from the front, device side of the wafer is not readily feasible with this process.

In this paper we examine two impurity sinks formed by ion implantation that combine large binding energies with the absence of a cut-off concentration, thereby satisfying the needs discussed above. The first is a microscopic cavity, formed by He implantation and annealing, whose reactive internal surfaces trap metal atoms by chemisorption. Such cavities are also nucleation sites for precipitation of bulk metal-silicide phases, so that this gettering mechanism is active as well when the solution is supersaturated. We have quantified the strength of cavity-wall chemisorption for Cu, Au, Co, and Fe. The second type of sink is a B-rich B-Si precipitate, formed by implanting B to a concentration above its solubility and annealing. Experiments on Fe and Cu impurities indicate that the metal atoms go into solution in the B_3Si phase with an energy substantially lower than in the Si phase.

The cavity and B-Si sinks share a property that should result in trapping no matter how small the pre-gettering concentration, unlike gettering based on metal-silicide precipitation. This property is the segregation of metal atoms to pre-existing low-energy sites, which at small impurity concentrations leads to a configurational-entropy term in the metal chemical potential of $kT\ln(\theta)$, θ being the fractional site occupation. Since the chemical potential for metal atoms in solution in the Si lattice varies with the solution concentration, C_S , as $kT\ln(C_S)$, equilibrium between sinks and solution leads to a constant of proportionality between θ and C_S .

2. Gettering by cavities

Cavities have been shown by several groups to getter transition metals effectively, with

both chemisorption reaction and the precipitation of bulk silicide phases taking place at the internal surfaces [see, e.g., Refs. 4-10 and citations therein]. To predict gettering behavior quantitatively, knowledge of the underlying energetics is needed. For silicide precipitation it suffices to determine the temperature-dependent solubilities of the metals, and extensive data on this property are available [1,2,11]. In contrast, the literature provides little quantitative information on the strengths of the chemisorption reactions. For this reason, chemisorption binding on the cavity walls was the principal focus of the present study.

Before presenting experimental results, we outline the formalism used to describe the binding of metal atoms by chemisorption and silicide precipitation. The strengths of these reactions are expressed in terms of a Gibbs free energy change associated with the transfer of one metal atom from the bound state to interstitial solution,

$$\Delta G \equiv \Delta H - T\Delta S_{\text{ex}} . \quad (1)$$

Here ΔH is the change in enthalpy, and ΔS_{ex} is the residual change in entropy after the previously mentioned configurational contributions due to fractional occupation of multiple solution and cavity-wall sites are taken into account separately. In the usage of thermodynamics, ΔG might be termed a relative partial excess atomic Gibbs free energy of solution; herein we refer to it simply as the binding free energy. The solution concentration of metal atoms in equilibrium with cavity-wall chemisorption, $C_s[\text{cav}]$, is then given by

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

$$\cong \theta \exp(-\Delta G_{\text{cav}}/kT) \text{ for } \theta \ll 1 \quad (2b)$$

where C_s is expressed as atomic fraction and θ is the fractional occupancy of the trap sites.

Equation (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

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

Equations (1)-(3) describe thermodynamic equilibrium. They are also the basis for source terms

in the diffusion equation when the thermal evolution toward equilibrium system is modeled, as detailed elsewhere [5]. A central objective is then to evaluate ΔG_{cav} for gettering temperatures.

Figure 1 shows a cross-section transmission electron microscopy (TEM) image of cavities formed by He implantation and annealing. When He is implanted at room temperature to concentrations above a threshold of about 2 at.%, a dense distribution of nanometer-size bubbles results. Subsequent heating at temperatures ≥ 973 K causes 1) diffusion of He from the cavities, 2) coalescence, enlargement, and faceting of the resulting voids, and 3) extensive annealing of implantation damage [12]. The internal surfaces of such cavities are initially pristine and are highly reactive as a result of dangling bonds. The cavity wall area is typically several times the specimen area.

Concentration profiles exhibiting the gettering of Co and Au by cavities are shown in Fig. 2. In both cases, the source of metal atoms was an excess of the equilibrium metal-silicide phase, formed at a different depth by implantation and annealing prior to the introduction of the cavities. This procedure is expected to stabilize the solution concentration at the solubility during subsequent gettering anneals. Confirmation was obtained for Fe by deep-level transient spectroscopy (DLTS): after annealing at 1223 K, DLTS indicated a solution concentration about 20% below the published value [11], within combined uncertainties. By thus preventing supersaturation, gettering due to silicide formation in the cavities was avoided, leaving only the wall-chemisorption reaction of interest.

The profiles in Fig. 2 illustrate the two types of cavity-gettering behavior that we observed in studies of Cu, Au, Co, and Fe impurities in equilibrium with the metal-silicide phase. In the case of Cu and Au, the acquisition of metal atoms continued until the areal density corresponded to about one monolayer (ML) on the cavity walls [5,12]. In contrast, the areal densities of gettered Co and Fe corresponded to wall coverages of <0.01 ML. These observations can be related to gettering energetics by combining Eqs. (2a) and (3) through use of the equilibrium condition $C_s[\text{cav}] = C_s[\text{sil}]$ to obtain

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

The fact that $\theta \approx 1$ for Cu and Au means that $\Delta G_{\text{cav}} \gtrsim \Delta G_{\text{sil}}$ for these metals, whereas the observation that $\theta \ll 1$ for Co and Fe implies $\Delta G_{\text{cav}} < \Delta G_{\text{sil}}$.

To obtain $\Delta G_{\text{cav}}[\text{Co}]$ and $\Delta G_{\text{cav}}[\text{Fe}]$, we experimentally determined θ for cavities in equilibrium with excess metal silicide, took $\Delta G_{\text{sil}}[\text{Co}] = 2.83 \text{ eV} - 7.6 \text{ kT}$ and $\Delta G_{\text{sil}}[\text{Fe}] = 2.94 \text{ eV} - 8.2 \text{ kT}$ from the literature [11], and substituted the results into Eq. (4). The fractional wall occupancy θ was equated to the measured areal density of gettered metal atoms divided by the areal density of cavity-wall chemisorption sites, the latter quantity being evaluated from analysis of TEM images TEM [12]. The binding free energies so obtained are plotted in Fig. 3.

Because these experiments did not employ rapid quenching after the high-temperature anneals (initial cooling rate $\approx 150 \text{ K/min}$), we used diffusion modeling [5] to assess possible changes in the metal content of the cavity layer during cooling. The only potentially significant effect found was gettering of metal atoms left in solution in the bulk of the specimen, and then only for Fe at the highest gettering temperature, 1273 K. In this case, the additional gettering of Fe during cooling could conceivably range from a negligible quantity to approximately the total measured amount, depending on the density of bulk sites for competing nucleation and growth of the silicide phase. Based on independent observations indicating a significant density of such bulk sites, this potential source of error at 1273 K was neglected.

Since the quantitative determination of ΔG_{cav} from Eq. (4) becomes unfeasible when θ approaches 1, a different, more elaborate approach was required for Cu and Au. In these cases, Rutherford backscattering spectrometry (RBS) was used to observe the diffusive redistribution of metal atoms between two cavity layers, one containing chemisorbed metal atoms at zero time and the other being initially unoccupied. The θ dependence in Eq. (2) gives rise to a difference in local solution concentration, ΔC_s , from one layer to another when $\theta_1 \neq \theta_2$, and this difference causes an interlayer diffusion flux, Φ , which in the limit of steady-state diffusion is given by

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

where D is the metal diffusion coefficient, N_{Si} is the atomic density of Si, and Δx is the average interlayer diffusion distance. When θ_2 is measured a function of time and D is taken from the

literature [11], ΔG_{cav} can be extracted using Eqs. (2a) and (5). An analogous procedure yields ΔG_{sil} , the measured flux in this case being that from a silicide-containing layer to a cavity layer. Equation (5) is again applicable, and when the cavity sinks bind substantially more strongly than the silicide, one has $\Delta C_s \approx C_s[\text{sil}] = \exp(-\Delta G_{\text{sil}}/kT)$. We used this procedure to obtain ΔG_{sil} for Cu and Au, where the previously available information is less precise than for Co and Fe.

The interlayer redistributions are illustrated by the results for Au in Fig. 4, where the areal density of metal atoms in the initially unoccupied cavity layer is plotted versus anneal time. The transfer from silicide to cavity sinks exhibits an abrupt saturation at a level corresponding within experimental uncertainty to 1 ML on the cavity walls, with a modest 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 more continuous fashion. A further noteworthy feature of the cavity-to-cavity redistribution is that, 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 (5); this is apparent in Fig. 4(b), where 50% of the implanted Au dose is about $7 \times 10^{15} \text{ cm}^{-2}$. The departure from 50% disappeared when the dose of implanted Au was reduced by a factor of five, leading us to hypothesize that the cause was ordered islands of chemisorbed Au coexisting with random-site chemisorption on the cavity walls. This is envisioned as occurring 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 at 923 and 973 K.

The theoretical curves in Fig. 4 were calculated using a numerical solution of the diffusion equation with source terms based on Eqs. (2a) and (3) as described elsewhere [5] rather than employing the tutorial simplifications of Eq. (5). The diffusion coefficient was taken from the literature [11], while the binding free energies were treated as adjustable parameters. The treatment was extended from Ref. 5 to include the hypothesized effects of ordered-island

chemisorption [13], 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 and Au are plotted in Fig. 3 with the previously discussed findings for Co and Fe. (In the case of Au chemisorption, the plotted values are for islands coexisting with random-site chemisorption. They are slightly higher than for random-site chemisorption alone.) These results allow the prediction of gettering behavior. Two prominent trends are apparent, and both can be qualitatively understood on physical grounds. First, $\Delta G_{\text{cav}} > \Delta G_{\text{sil}}$ for Cu and Au, whereas the opposite is true for Co and Fe. This is ascribed to the fact the monovalent metals can optimize their bonding by reacting with the single dangling orbitals on 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, most of the energies trend upward with decreasing temperature, consistent with a positive value of $T\Delta S_{\text{ex}}$. We hypothesize that this reflects 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 network. The exceptions to this trend occur for chemisorbed Cu, where the range of data is too limited to establish a temperature dependence, and for the precipitated Si-Au phase, which is molten at the anneal temperatures and therefore expected to have a relatively high entropy.

3. Gettering by precipitated boron silicide

When implantation of B into Si is followed by annealing at a temperature where the B is both mobile and supersaturated, the concentration profile exhibits a central peak at the implantation range with wings on either side [see, e.g., Ref. 14]. An example from our work of this widely reported phenomenon is seen in Fig. 5(a). The generally recognized cause is precipitation of a B-Si phase at the central peak accompanied by defect-enhanced diffusion of B in the Si lattice at concentrations below the solubility. When the implanted concentration is less

than the solubility, the enhanced-diffusion broadening occurs without a precipitation-related peak, as seen in Fig. 5(b). The unprecipitated B is substitutional and is a shallow acceptor. The negatively charged B atoms trap Fe impurities through formation of B^-Fe^+ pairs with a binding energy of about 0.65 eV [15], and at higher B concentrations the attraction relative to the unimplanted Si substrate can be augmented by several additional tenths of an eV due to band bending [16]. The resulting gettering, while relatively modest in strength, has been shown to remove Fe impurities from solution during cooling from elevated temperatures [16].

We are exploring the gettering of metal atoms by the precipitated B-Si phase, with initial experiments being performed on Fe and Cu impurities. The experimental approach parallels that used to examine cavity gettering of Co and Fe, with SIMS being employed to measure the number of gettered metal atoms in equilibrium with remotely located precipitates of the metal-silicide phase. Use of the known thermodynamic properties of the silicides then permits the strength of the metal reactions with the B-Si phase to be assessed, as for cavity trapping.

Selected results from our experiments on Fe are shown in Fig. 5. Before B was implanted, excess $FeSi_2$ was formed on the opposite side by implantation of Fe and annealing. As a result, the solution concentration of Fe was stabilized at the solubility during the gettering anneal at 1273 K. The profiles in Fig. 5(a) exhibit an association of Fe with the B, but only in the region of B-Si precipitation. Furthermore, the similarity of B and Fe peak shapes in the figure suggests that the concentration of gettered Fe scales with the amount of precipitated B, and this is confirmed by plotting the depth profiles with a linear concentration scale. It thus appears that Fe is gettered more strongly by the B-Si precipitates than by substitutional B, and the scaling of B and Fe concentrations leads us to propose that the bound Fe resides in solution in the B-Si phase. Similar experiments were carried out for Cu impurities with analogous results, the amount of gettered Cu being about an order of magnitude larger.

Figure 6(a) shows a TEM micrograph of Si after high-dose B implantation and annealing at 1373 K, and B-Si precipitates ~ 10 nm in size are apparent. Compositional analysis of these particles using electron energy loss spectroscopy (EELS) indicates that they are B rich, with a B-

to-Si atomic ratio near 2.5 or somewhat greater. No evidence of crystallinity in the B-Si phase was found by electron diffraction, bright-field contrast, or lattice imaging; moreover, lattice images, such as the one in Fig. 6(b), exhibit the irregular granularity characteristic of solids lacking long-range structural order. (The TEM specimen was thinned chemically rather than by ion milling to avoid amorphization by the latter treatment.) Since 1373 K is the highest temperature of this study, we conclude that the observed gettering occurred in a disordered phase of approximate composition B_3Si .

When initially supersaturated Si(B) reaches full thermodynamic equilibrium at temperatures $\lesssim 1543$ K, the Si host phase is believed to coexist with a crystalline phase of approximate composition B_3Si [17,18]. Like many B-rich solids, B_3Si has a complex structure based on icosahedral units at the corners of a large rhombohedral cell with additional atoms along the three-fold axis of the cell. Boron-rich structures of this kind have several characteristics that are expected to promote the incorporation of transition-metal atoms; these include the strong electron affinity and high stability of the icosahedral units, the presence of relatively large open volumes outside the icosahedra, and the considerable variability and flexibility of the overall structure and bonding configuration [19,20]. In such a material, transition metals can be expected to serve as electron donors and to reside in the high-volume interstices with relatively little steric hindrance.

Although the B-Si precipitates of the present experiment apparently lack long range order, we hypothesize that the local bonding and structure are similar to those of crystalline B_3Si . Indications of this include the similarity of composition and the near coincidence of chemical potentials; the latter property is inferred from the observation that the diffusion tails in the B depth profiles, such as the one in Fig. 5(a), intersect the central peak at a concentration equal within experimental uncertainty to the published equilibrium solubility. That the precipitates do not attain full long-range order after 2 h at 1373 K is not surprising in view of the structural complexity and highly refractory character of B-rich solids and the small precipitate size. Based on these considerations, we provisionally interpret the observed gettering of Fe and

Cu as arising from solution of the metal atoms in the precipitated, disordered B-Si phase, this process being promoted by the properties of B₃Si discussed above.

Figure 7 shows an Arrhenius plot of the ratio of gettered metal atoms to precipitated B atoms in equilibrium with metal-silicide phase at a different depth, usually on the opposite side of the wafer. The areal density of precipitated B was evaluated by integrating the central peak of the depth profile after subtraction of the solution concentration. Results are shown for two doses of implanted B that differ by a factor of 5, and the consistency of the ratio between these doses reinforces the inference of scaling between gettered-metal concentration and the amount of precipitated phase. Diffusion modeling indicates that changes in the amount of gettered metal during cooling after annealing should not have significantly perturbed these results.

With the above interpretation, and if in addition the metal-binding sites within the B-Si phase are assumed to be of a single type and not to interact with one another, Eq. (2) is applicable. Although the actual number of available sites is not yet known and θ can therefore not be evaluated, if the sites are far from saturation Eq. (2b) can be modified to obtain

$$C_s \cong \alpha \{ \Lambda_{M,gett} / \Lambda_{B,ppt} \} \exp(-Q/kT) \quad (6)$$

where α is a constant, $\Lambda_{M,gett}$ is the areal density of gettered metal atoms, $\Lambda_{B,ppt}$ is the areal density of precipitated B, and Q is an activation energy. While the levels of Cu in Fig. 7 may or may not correspond to site saturation, it seems plausible that the much smaller quantities of Fe do not. We therefore apply Eq. (6) to Fe: using the fitted line through the Fe data in Fig. 7 and Eq. (3) with $\Delta G_{sil}[Fe] = 2.94 \text{ eV} - 8.2 \text{ kT}$ gives $\alpha = 6100$ and $Q = 2.21 \text{ eV}$. This result allows the extent of Fe gettering to be predicted so long as the sinks are unsaturated.

As a test of the linear dependence of C_s on $\{ \Lambda_{M,gett} / \Lambda_{B,ppt} \}$ in Eq. (6), we performed an additional experiment on Fe gettering where silicide was not introduced to stabilize the solution concentration at the solubility, so that only pre-existing Fe was present. After the gettering anneal at 1273 K, SIMS profiling showed a decrease in $\{ \Lambda_{M,gett} / \Lambda_{B,ppt} \}$ from the silicide-buffered experiments of about a factor of 6, while DLTS indicated that the final solution concentration was about one tenth of the published solubility. This semiquantitative consistency

is within the combined experimental uncertainties.

4. Prediction of gettering performance

The implications of our findings for the effectiveness of gettering by cavities and B-Si precipitates are illustrated in Fig. 8, where model calculations based on Eqs. (2a), (3), and (6) are shown. A wafer a thickness of 0.5 mm was assumed to contain initially a uniform concentration of Fe or Cu in solution. The gettering proceeded to equilibrium at 973 K, a temperature where metal-atom mobilities are still sufficient to sweep the wafer. The assumed areal density of cavity-wall sites was $5 \times 10^{15} \text{ cm}^{-2}$, and the areal density of precipitated B was $1 \times 10^{17} \text{ cm}^{-2}$, both typical values. The solution concentration after gettering is plotted in Fig. 8 as a function of the initial concentration. The curves for cavity gettering include the effect of silicide precipitation when the solution concentration exceeds the solid solubility. The gettering by B-silicide particles was not extended into this regime; although these precipitates may also support nucleation of the metal silicides, this has still to be demonstrated.

A noteworthy aspect of these computational results is the substantial gettering for initial impurity concentrations below the threshold for silicide precipitation: the concentration reduction is two orders of magnitude even for Fe in cavities, the least favorable case. When this finding is considered in conjunction with the demonstrated microstructural stability of the two gettering centers above 1300 K and the anticipated feasibility of gettering on the device side as well as the back side of wafers, technological application appears potentially attractive.

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Figure captions

1. Cross-section TEM image of cavities. The (100)-Si specimen was implanted with 1×10^{17} He/cm² at 30 keV and then vacuum annealed at 1173 K for 1 h. The image was obtained with -600 nm defocus to highlight the cavities with Fresnel contrast.
2. Depth profiles of Co and Au chemisorbed on cavity walls. The Co sample was implanted with 5×10^{15} Co/cm² at 623 K and 100 keV and then annealed at 873 K for 1 h and at 1173 K for 2 h to develop the CoSi₂ phase. It was subsequently implanted with 1×10^{17} He/cm² at 150 keV on the opposite side and annealed at 1173 K for 2 h to form cavities and induce the gettering seen in the profile. The Au-containing sample was implanted with 1×10^{16} Au/cm² at 300 keV, annealed at 1123 K for 2 h to precipitate the silicide, implanted with 1×10^{17} He/cm² at 150 keV on the same side, and annealed at 1023 K for 50 h to form cavities and induce gettering.
3. Binding free energies relative to solution of transition metals chemisorbed on cavity walls and precipitated as equilibrium silicide phases.
4. Diffusive redistribution of Au between silicide and cavity layers. The conditions for silicide-to-cavity redistribution were as described for Fig. 2. In the case of cavity-to-cavity redistribution, the two cavity layers were formed prior to Au injection by implanting 1×10^{17} He/cm² at both 30 and 180 keV and annealing at 1173 K for 1 h. The Au was subsequently implanted on the same side at 300 keV to a dose of 1.5×10^{15} cm⁻².
5. Depth profiles of implanted B and of Fe getterred to the B from the FeSi₂ phase. Iron was implanted at 623 K and 100 keV to a dose of 5×10^{16} cm⁻², followed by annealing at 793 K for 1 h and at 1273 K for 2 h to develop the FeSi₂ phase. Boron was then implanted on the opposite side at 300 keV, and the specimens were annealed at 1273 K for 2 h to cause B precipitation and gettering of the Fe. The B implantation doses were (a) 2.5×10^{16} cm⁻² and (b) 2.5×10^{15} cm⁻².
6. Transmission electron microscopy of B-Si precipitates in (100)-Si. (a) Bright-field plan-view image. (b) [110] Si lattice image.

7. Atomic ratio of gettered Fe and Cu to precipitated B under conditions of equilibrium with excess metal-silicide phase at a different depth.
8. Predicted gettering of Fe and Cu by cavities and B-Si precipitates.

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1

2

6

(a)

(b)

8