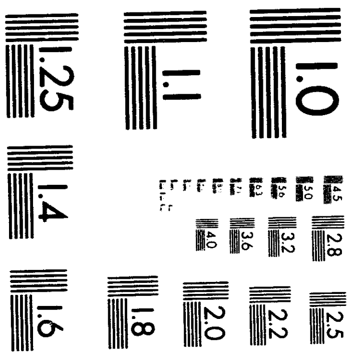

SAND93-1453C
Conf-931108--7

BINDING OF COPPER AND NICKEL TO CAVITIES IN SILICON FORMED BY HELIUM ION IMPLANTATION

S.M. MYERS, D.M. FOLLSTAEDT, AND D.M. BISHOP
Semiconductor Physics Dept. 1112, Sandia National Laboratories, Albuquerque, NM 87185-1056

ABSTRACT

Cavities formed in Si by He ion implantation and annealing are shown be strong traps for Cu and Ni impurities. Experiments utilizing ion-beam analysis and transmission electron microscopy indicate that Cu is trapped at the internal surfaces of cavities up to ≈1 monolayer coverage with a binding energy of 2.2±0.2 eV relative to solution. This is greater than the heat of solution from the precipitated Cu_3Si phase, determined to be 1.7 eV in agreement with earlier work. Copper at cavity-wall sites is reversibly replaced by H during heating in H_2 gas, indicating the relative stability of the two surface terminations. Initial results for Ni impurities indicate that trapping at cavities is again energetically preferred to silicide formation. The saturation coverage of Ni on the internal surfaces, however, is an order of magnitude smaller for Ni than Cu, consistent with published studies of external-surface adsorption. These results suggest that cavity trapping may getter metallic impurities in Si more effectively than methods based on silicide precipitation.

INTRODUCTION

Transition-metal impurities are extremely detrimental in Si-based microelectronics, introducing deep levels into the band gap and precipitating at such undesirable locations as Si-SiO_2 interfaces. Moreover, because these elements are highly mobile in Si, growing precipitates can draw metal atoms from a macroscopic wafer volume. (For a review, see Ref. 1.) The concern with Cu impurities in particular is amplified by the prospect of Cu metallization in devices [2]. In device production, stringent clean-room procedures are supplemented by gettering, a procedure whereby metal impurities are tied up in sacrificial regions of the wafer. Gettering is most often accomplished by introducing imperfections such as SiO_2 precipitates and lattice defects, which nucleate silicide precipitation [1]. Also used is P doping, believed to enhance the solubility of the impurity in the doped region [1]. Ion implantation has been an important tool for the introduction of gettering centers for more than 20 years. (See, e.g., Ref. 3.)

In the present work we mechanistically investigated the trapping of two transition metals, Cu and Ni, at the internal surfaces of cavities formed in Si by He ion implantation and annealing. Particular attention was given to the strength of trapping and the number of binding sites. Internal surfaces are highly reactive due to the Si dangling orbitals and may bind metal impurities even more strongly than precipitates of the metal silicide phases. Furthermore, while second-phase precipitation reduces the solution concentration to a characteristic solid solubility and no further, the influence of static traps such as surface dangling bonds should persist to arbitrarily small concentrations. Therefore, cavity traps may provide an attractive alternative for gettering. While the structures of transition-metal adsorbates on external Si surfaces have been investigated extensively, with detailed information being available for both Cu [4,5] and Ni [6,7], quantitative information on binding energies relative to solution and to the silicide phases was lacking before the present study. The results reported here are final in the case of Cu but preliminary for Ni.

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

METHOD

Cavities were formed in Si by ion implanting He at room temperature and then vacuum annealing at 700 or 900°C, a procedure similar to one reported previously [8]. The anneal caused release of the He from the Si [8], removed implantation damage, and enlarged the cavities. Copper and Ni were then introduced by ion implantation, and precipitation of the respective equilibrium silicides was induced by annealing. The interactions of the metal solutes with the cavities in such specimens were examined by positioning the cavity and silicide layers at different depths and observing the internal redistributions of the Cu or Ni by Rutherford backscattering spectrometry (RBS). In experiments involving H, the deuterium isotope was employed and profiled using the ion-beam-induced nuclear reaction $^2H(^3He,^1H)^4He$ [9]. The microstructure of the cavities was determined using transmission electron microscopy (TEM), and the presence of the Cu_3Si phase was demonstrated by transmission electron diffraction as discussed elsewhere [10].

To extract binding energies from the above experiments, we numerically solved the coupled differential equations which describe diffusion accompanied by reversible trapping and second-phase precipitation and adjusted the binding energies to produce agreement with the data. The methodology of such calculations has been described elsewhere [11] and will not be repeated here. Instead, to convey the physical basis of the analysis, we present simplified equations that approximately describe the two types of experiment reported in the following section. The first of these is the transport of metal atoms from a silicide phase at one depth to cavity traps at another depth. If the traps are sufficiently strong to be regarded as irreversible, and if the cavity and silicide layers are assumed to have negligible thickness and to be separated in depth by Δx, then the steady-state diffusion flux, Φ, is given by

$$\Phi \approx n_s D/\Delta x \qquad (1)$$

where n_s is the solubility of the metal in equilibrium with the silicide phase expressed as atomic density and D is the diffusion coefficient. When the diffusion coefficient in Eq. (1) is taken from the literature, the measured redistribution flux gives the solubility, and the temperature dependence of this solubility then determines the heat of solution from the silicide phase.

The second type of experiment involves redistribution between two cavity layers, one initially saturated with metal atoms and the other initially unoccupied. The redistribution leads ultimately to equal fractional occupations of traps in the two layers. The flux of metal atoms, with simplifying assumptions similar to those made above, is

$$\Phi \approx [n_c(\theta_1) - n_c(\theta_2)]D/\Delta x \qquad (2)$$

where $n_c(\theta)$ is the solution concentration in *local* equilibrium with the cavity traps in layer 1 or 2 and θ is the fractional occupancy of the trapping sites. The quantity n_c is given by

$$n_c(\theta)/N_s \approx [\theta/(1-\theta)]\exp(-E_c/kT) \qquad (3)$$

where N_s is the temperature-independent atomic density of solution sites and E_c is the trap binding energy relative to solution. Hence, the experimentally measured flux Φ is sensitive to the binding energy.

RESULTS AND INTERPRETATION

Figure 1 shows a cross-section TEM image of cavities formed by implanting 10^{17} He/cm^2 at room temperature and 30 keV and then vacuum annealing for 30 min at 700°C. Detailed analysis of such images indicates that the average cavity diameter is 8 nm and that the ratio of internal surface area to wafer area is 6.7±1.2. The latter number implies that there are $\approx 5\times10^{15}$ Si atoms on the internal surfaces per cm^2 of wafer area. The cavities are faceted, with (111) faces predominating followed in order by (100) and (110) [12].

The binding of Cu to such cavities was demonstrated by forming the equilibrium silicide η-Cu_3Si on the opposite side of the 250-μm thick Si sample and then observing the diffusion of Cu from the silicide across the wafer to the cavities during vacuum annealing. The silicide was introduced by implanting 10^{17} Cu/cm^2 at 150 keV and then annealing at 600°C, and its presence was demonstrated by transmission electron diffraction [10]. During more extended annealing at 600°C, the silicide partially dissolved and the Cu diffused to the cavities until the associated internal surfaces were saturated. The saturation depth profile of Cu, as measured from the cavity side of the specimen, is given by open circles in Fig. 2. The consistency of the profile with the depth distribution of cavities is apparent. The saturation areal density of Cu in the cavity layer is 5×10^{15} cm^{-2}, corresponding to about one monolayer on the internal surfaces.

When the dose of implanted He was reduced to 2×10^{16} cm^{-2}, TEM showed that the cavities were several times fewer in number and restricted to a narrower band about the peak He concentration, whereas at a dose of 1×10^{16} He/cm^2 there were only a few isolated cavities. The saturation depth profiles for these cases are included in Fig. 2 and are seen to reflect the variations in observed microstructure. The cavity microstructure was also changed by annealing at 900°C for 1 hr instead of 30 min at 700°C after implanting 10^{17} He/cm^2. The cavities were then observed to be larger, with an average diameter of about 20 nm, and fewer in number, leading to a

Fig. 1. Cross-section TEM of cavities in Si. The depth scale conforms to that of Fig. 2.

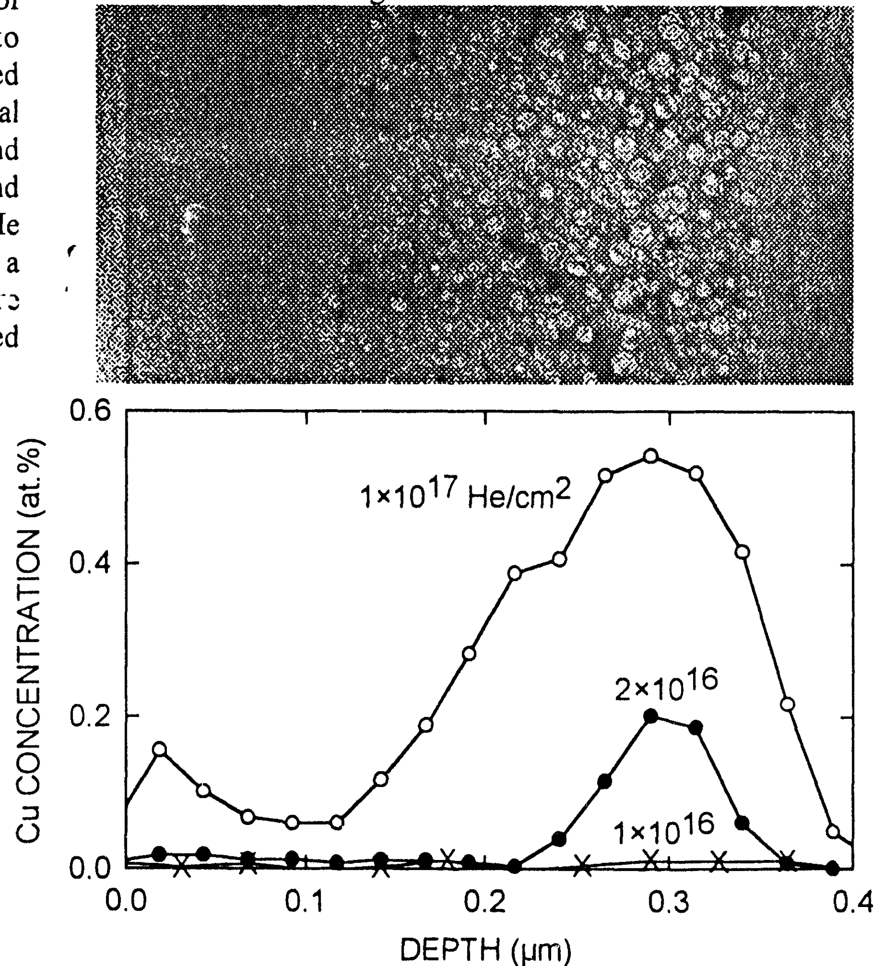

Fig.2. Saturation depth profiles of Cu in cavities.

reduction of about 50% in the internal surface area. Consistent with this change, the saturation areal density of Cu decreased to 2.3×10^{15} cm^{-2}. These comparisons reinforce the view that the trapped Cu is indeed occupying surface sites on the cavity walls.

The transfer of Cu from the silicide to the cavity layer demonstrates that the binding on the internal surfaces is more stable. To quantify the respective binding energies, we examined the rates of internal Cu redistribution in multilayered specimens as outlined in the preceding section. For example, Fig. 3 shows the accumulation of Cu in cavities resulting from silicide dissolution under two conditions. In one of these, the Cu_3Si and cavities were on opposite sides of the wafer and separated by 250 μm, and the isothermal annealing was performed at 600°C. In the other case, the silicide and cavity layers were on the same side of the wafer and were respectively centered at 0.1 and 0.7 μm, so that the separation was ≈0.6 μm. The resulting much smaller value of Δx in Eq. (1) was offset by performing the isothermal anneals at the lower temperature of 450°C, where the solubility n_s and diffusion coefficient D are greatly reduced, so that the rate of Cu redistribution was comparable at the two temperatures. The theoretical curves in Fig. 3 were obtained by solving the diffusion-trapping-precipitation formalism of Ref. 11, using the published diffusion coefficient for Cu in Si [13] and adjusting the solubilities at 450 and 600°C to produce agreement with experiment. The fitted solubilities are 1.7×10^{12} cm^{-3} at 450°C and 2.0×10^{14} cm^{-3} at 600°C, giving a solution activation energy of 1.73 eV, in good agreement with earlier studies of Si-Cu_3Si equilibrium above 650°C [14].

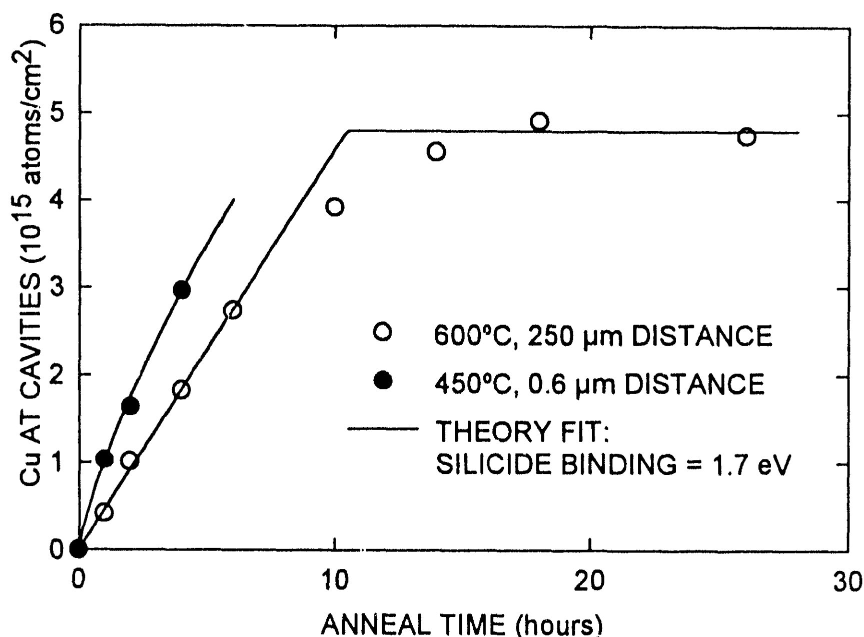

Fig. 3. Redistribution of Cu from Cu_3Si to cavities.

To determine the binding energy for Cu in cavity traps, samples were prepared with two cavity layers, one initially saturated with Cu and the other initially unoccupied. Then, during isothermal annealing at 650 or 700°C, the redistribution between the layers leading to equilibration of trap occupancies was followed as a function of time. The redistribution rate is sensitive to the cavity-trap binding energy as discussed in the preceding section. The starting condition for the isothermal anneals was created by 1) forming the first cavity layer at a depth of 0.7μm, 2) saturating it with Cu by heating in the presence of silicide located at 0.1 μm, 3) evaporating the Cu from the excess silicide by heating for 3 hours at 800°C, and 4) forming the second cavity layer at 0.3 μm. Figure 4 shows the accumulation of Cu in the second cavity layer as a function of time at the two temperatures. The curves represent solutions of the diffusion-trapping formalism of Ref. 11 in which the binding energy was adjusted to agree with the data. This procedure yielded 2.2±0.2 eV expressed relative to Cu in solution. The binding energy within the cavity traps is thus ≈0.5 eV larger than the solution activation energy for Cu_3Si.

A significant issue for the use of cavities as metal-impurity traps is the possibility of

competition for the binding sites by H, which can be introduced into Si at various stages of device processing. A previous study determined that the binding energy of H on cavity surfaces relative to H_2 gas is 0.37 ± 0.1 eV [15]. Since the binding energy obtained above for Cu in cavities relative to Cu_3Si is ≈ 0.5 eV, the two quantities differ by substantially less than the combined uncertainties. Hence, whether Cu from the silicide or H from H_2 gas preferentially occupies the cavity surfaces is not established by information presented to this point. We therefore performed an experiment to observe the competition directly. Cavities were formed by implanting 10^{17} He/cm^2 at 30 keV and annealing for 30 min at 700°C. The surfaces of these cavities were then saturated with Cu by heating at 600°C in the presence of excess Cu_3Si on the opposite side of the specimen. The resulting saturation areal density was 5.2×10^{15} Cu/cm^2. The specimen was subsequently heated in H_2 gas at 600°C and a pressure of 650 Torr for 113 hours, a condition previously shown to saturate the walls of initially unoccupied cavities without producing a significant quantity of H_2 gas within the open volume [9]. This treatment decreased the Cu content of the cavities to 0.5×10^{15}cm^{-2}, and H accumulated in the cavity layer to an areal density of 7.6×10^{15} cm^{-2}. A final vacuum anneal of 1 hour at 800°C reduced the H content by about 90% and restored the Cu areal density to 6.4×10^{15} cm^{-2}, indicating reversibility. Thus, H occupies the cavity-surface sites in preference to Cu for these conditions. We hypothesize that the observed replacement of one Cu atom by more than one H atom is a consequence of the Cu undergoing strong chemisorption only on the predominant (111) facets. This is consistent with studies of Cu on external (111) and (100) surfaces [4,5]. One implication of these results is that H should be outgassed before using cavities for trapping of metals.

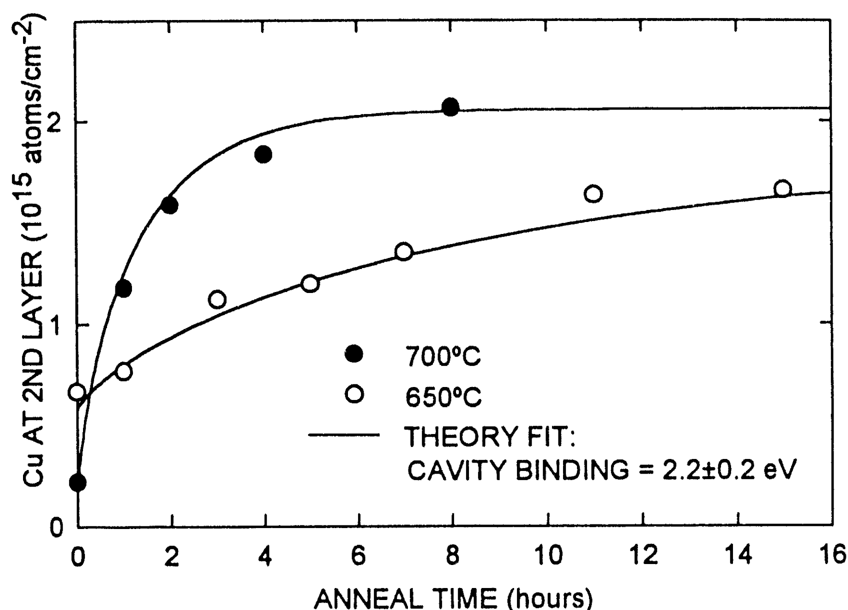

Fig. 4. Redistribution of Cu from an initially saturated cavity layer to a second, initially unoccupied cavity layer.

We also performed preliminary experiments on the trapping at Si cavities of Ni, another technologically important metal impurity. The cavities were formed on one side of a 250µm-thick specimen by implanting 10^{17} He/cm^2 at 30 keV and annealing at 900°C for 1 hour. Nickel was then implanted on the opposite side at 150 keV and a dose of 10^{17} cm^{-2}. The material was subsequently annealed for 89 hours at 550°C, then for 24 hours at 600°C, and finally for 16 hours at 700°C. The time at each temperature was more than sufficient to transfer 10^{16} Ni/cm^2 from precipitated silicide across the sample to sinks, based on estimates using published diffusion coefficients and solubilities [13]. The measured areal density of Ni in the cavity layer was 0.18×10^{15} cm^{-2} after the first anneal and remained constant during the subsequent heat treatments. We provisionally interpret these results as indicating that Ni, like Cu, is bound more strongly on the cavity walls than in the metal-silicide phase. The greatly reduced saturation areal density for Ni in the cavity layer — the value is 2.3×10^{15} cm^{-2} for Cu under equivalent

conditions — is tentatively ascribed to the much less dense ordered structure of chemisorbed Ni on (111) Si. In particular, on external (111) surfaces, ordered chemisorption of Cu is observed to reach ≈1 monolayer before silicide formation [4], whereas the ordered structure of Ni is a $\sqrt{19}\times\sqrt{19}$ configuration with a maximum coverage of at 1/19 monolayer [6]. On the (100) surface, the tendency for chemisorption is apparently much less for both metals [5,7].

CONCLUSION

We have shown that two of the detrimental transition-metal impurities in Si, Cu and Ni, are trapped by microscopic cavities sufficiently strongly not only to remove atoms from solution but also to dissolve pre-existing silicides. These cavities are thermally stable, surviving heating to temperatures as high as 1180°C [16]. Moreover, their formation by He ion implantation is potentially feasible on the device side as well as the back side of wafers. Because of these properties, cavities are potentially attractive gettering centers for metal impurities in Si.

ACKNOWLEDGMENT

The authors benefited greatly from discussions with H. J. Stein, J. W. Medernach, P. A. Bennett and R. B. Doak. This work was supported by the United States Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract DE-AC04-94AL85000.

REFERENCES

1. W. Schröter, M. Seibt, and D. Gilles, in Materials Science and Technology 4: Electronic Structure and Properties of Semiconductors, edited by W. Schröter (VCH Publishers., New York, 1991) pp. 539-589.
2. MRS Bulletin **18**, No. 6 (June 1993).
3. T.M. Buck, K.A. Pickar, and J.M. Poate, Appl. Phys. Lett. **21**, 485 (1972).
4. D.D. Chambliss and T.N. Rhodin, Phys. Rev. B **42**, 1674 (1990), and references therein.
5. H. Kemmann, F. Müller, and H. Neddermeyer, Surf. Sci. **192**, 11 (1987).
6. R.J. Wilson and S. Chiang, Phys. Rev. Lett. **58**, 2575 (1987).
7. A.E. Dolbak, B.Z. Olshanetsky, S.I. Stenin, and S. A. Teys, Surf. Sci. **218**, 37 (1989).
8. C.C Griffioen, J.H. Evans, P.C. de Jong and A. Van Veen, Nucl. Instrum Meth. **27**, 417 (1987).
9. S.M. Myers, D.M. Follstaedt, H.J. Stein, and W.R. Wampler, Phys. Rev. B **47**, 13380 (1993).
10. D.M. Follstaedt and S.M. Myers, present symposium proceedings.
11. S.M. Myers and D.M. Follstaedt, J. Appl. Phys. **65**, 311 (1989).
12. D.M. Follstaedt, Appl. Phys. Lett. **62**, 1116 (1993).
13. E.R. Weber, Appl. Phys. A **30**, 1 (1983).
14. R.C. Dorward and J.S.Kirkaldy, Trans, Met. Soc. AIME **242**, 2055 (1968).
15. W.R. Wampler, S.M. Myers, and D.M. Follstaedt, Phys. Rev. B **48**, 4492 (1993).
16. J.W. Medernach (private communication).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DATE
FILMED
1/12/94

END