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Citation: *Applied Physics Letters* **88**, 222107 (2006); doi: 10.1063/1.2208382

View online: <http://dx.doi.org/10.1063/1.2208382>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/88/22?ver=pdfcov>

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## Trapping of Pd, Au, and Cu by implantation-induced nanocavities and dislocations in Si

D. A. Brett,<sup>a)</sup> D. J. Llewellyn, and M. C. Ridgway

*Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, Australian National University, Canberra, Australian Capital Territory 0200, Australia*

(Received 25 March 2006; accepted 18 April 2006; published online 31 May 2006)

The gettering of metallic impurities by nanocavities formed in Si is a topic of both scientific importance and technological significance. Metallic precipitates observed in the regions where nanocavities were formed have been considered the result of the metal filling the nanocavities, either as elemental metal or a silicide phase. However, our transmission electron microscopy observations demonstrate that many of these precipitates are concentrated along dislocations, rather than randomly distributed as expected for precipitates formed by the filling of nanocavities. Consequently, the gettering contribution of dislocations in the lattice caused by nanocavity formation must be considered. For Pd, dislocations are the preferred sites for the precipitation of the metal silicide. We compare results of gettering by nanocavities and dislocations for Pd, Au, and Cu to determine which structure is the dominant influence for the formation of precipitates of these metals and/or their silicides. © 2006 American Institute of Physics. [DOI: 10.1063/1.2208382]

Metallic contamination is detrimental to the performance of semiconductor devices, reducing the Si minority carrier lifetime and the SiO<sub>2</sub> breakdown voltage and introducing deep levels into the Si band gap.<sup>1</sup> Consequently, the gettering of these unintentionally introduced impurities has been the topic of extensive research. Nanocavity structures, produced in Si by the implantation of H or He and subsequent annealing, are capable of gettering a wide range of metals, including Fe,<sup>2</sup> Co,<sup>3</sup> Ni,<sup>4</sup> Cu,<sup>5</sup> Pd,<sup>6</sup> Ag,<sup>7</sup> Pt,<sup>8</sup> and Au.<sup>9</sup> Precipitates of these metals and/or their silicides have been frequently observed in nanocavity structures, and it has been assumed that these precipitates were the result of excess metal filling in the nanocavities. The use of dislocations as a gettering technique is also well established,<sup>10</sup> and they are commonly introduced intentionally using ion implantation. They are also produced as a consequence of nanocavity formation; however, the contribution of these dislocations to the gettering observed in nanocavity structures has not been investigated previously. Recently,<sup>6</sup> we observed that Pd-containing precipitates were concentrated along dislocations rather than being randomly distributed amongst nanocavities. To determine whether this effect was unique to Pd or common to other metals, Au and Cu were chosen for comparison. The gettering behavior of these two metals, both in nanocavities and on dislocations, has been extensively investigated in the past.<sup>11,12</sup> Samples were prepared containing either nanocavities (with the dislocations created during nanocavity formation) or dislocations alone, and the precipitate distributions have been compared.

Using P-doped 5–10 Ω cm (100) Czochralski Si, a nanocavity structure was formed by a room temperature implantation of  $3 \times 10^{16}$  cm<sup>-2</sup> H<sup>-</sup> ions at 30 keV and subsequent annealing at 850 °C for 1 h in an Ar ambient. In separate material, a band of dislocations was formed by Si<sup>+</sup> implantation at 260 keV to a dose of  $1 \times 10^{16}$  cm<sup>-2</sup> at 250 °C, followed by annealing at 850 °C for 1 h in an Ar ambient. The elevated Si implant temperature was chosen to

avoid the amorphization of the Si substrate. These implants produced either a nanocavity structure ~100 nm thick centered at a depth of ~350 nm with an average nanocavity diameter of ~10 nm, or a dislocation region ~400 nm thick centered at a depth of ~500 nm. (We note that the dislocations formed from the Si implantation were of a different density to those formed in the nanocavity structure.) The samples were then implanted with a dose of  $5 \times 10^{14}$  cm<sup>-2</sup> of Pd, Au, or Cu at energies of 230, 350, or 140 keV, respectively, giving a projected range for all metals of ~110 nm according to SRIM 2003.<sup>13</sup> These implantation profiles were shallower than either gettering structure. The samples were then annealed in Ar for 1 h either at 950 °C (Pd), 850 °C (Au), or 780 °C (Cu). These temperatures were chosen from those published in the literature to maximize the amount of metal trapped in the nanocavity structures,<sup>6,14</sup>

Secondary ion mass spectrometry (SIMS) with either 12 keV O<sub>2</sub><sup>+</sup> or 10 keV Cs<sup>-</sup> ions was used to determine the depth profile of the implanted metals. Transmission electron microscopy (TEM) was also performed at 300 kV in both cross section and plan view to examine the preferred precipitation location of the metals.

The proportion of Pd gettered to the nanocavity structure (~51%) was lower than that found for Au and Cu, where ~100% and ~92% of the implanted metal were located in the nanocavity structure, respectively, and these values are consistent with earlier reports. The Pd gettered in the sample containing dislocations accounts for only ~14% of the implanted Pd, compared with ~100% and ~43% for the Au- and Cu-containing samples, respectively. These results require some explanation. Firstly, the quantity of undetected Pd in the sample with dislocations is in excess of the published (approximate) Pd solid solubility at the annealing temperature.<sup>15</sup> The reverse is true for the other metals, where the gettering efficiencies were higher than expected. Such an efficient gettering of Au to dislocations is at odds with previously published data<sup>16</sup> that reported that samples with pre-existing dislocations did not getter as effectively as those where the dislocation network was formed during the diffu-

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: dab109@rsphysse.anu.edu.au

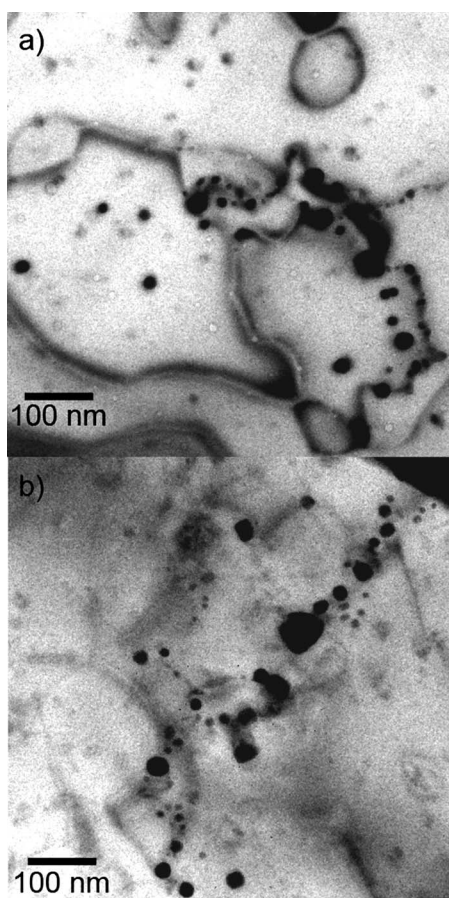


FIG. 1. Plan view TEM micrographs showing samples containing (a) Pd and nanocavities and (b) Pd and dislocations.

sion anneal. However, the results presented here are consistent with the Au solubility data, which indicate that the Au concentration in the sample is almost an order of magnitude above its solid solubility at this annealing temperature.<sup>15</sup> However, the published solubility data for Cu indicate that the solubility of Cu at 780 °C is greater than the total concentration of Cu implanted if equilibrated throughout the wafer,<sup>15</sup> suggesting that the dislocations should not be able to getter any Cu under these annealing conditions. The fact that the dislocations were so successful in trapping Au and Cu, to levels below the published solubility limit of these metals, can be explained by the initial supersaturation of metal caused by ion implantation.

Under TEM examination, the differences in the gettering behavior of Pd, Au, and Cu become apparent. In the sample containing Pd and dislocations, extended dislocations of up to a few microns in length were observed with many precipitates along their length. As shown in Fig. 1(a), these precipitates were tens of nanometers in diameter, which were determined by electron diffraction to be Pd silicides. In the samples containing Pd and the nanocavity structure, identical features could be observed, as shown in Fig. 1(b). The precipitates were crystalline, with a similar size range and consistently associated with dislocations. This suggests a strong preference for excess Pd precipitation on dislocations rather than inside nanocavities.

In contrast, in the samples containing either Au or Cu and nanocavities, we see numerous small, randomly distributed precipitates, examples of which from the Au sample are shown in Fig. 2(a). Cu-containing precipitates were noted to

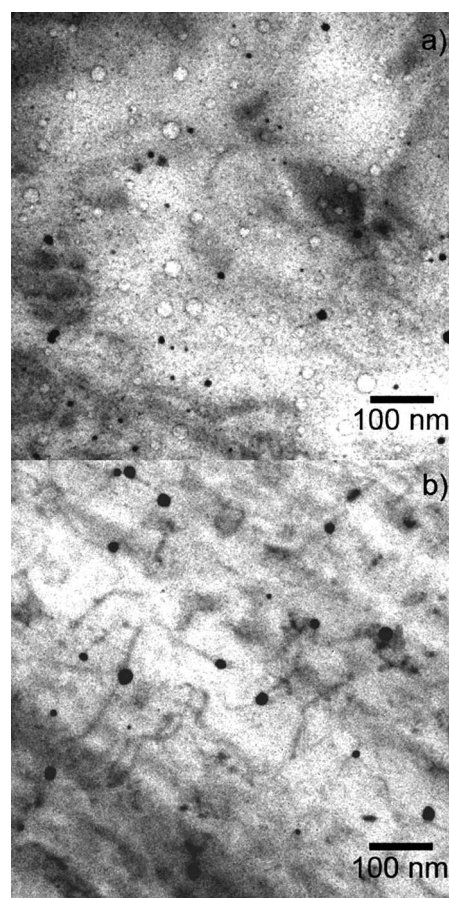


FIG. 2. Plan view TEM micrographs showing samples containing (a) Au and nanocavities and (b) Au and dislocations.

be larger than the Au-containing precipitates, most probably due to the presence of  $\text{Cu}_3\text{Si}$ , which was confirmed to be present by electron diffraction. The very few precipitates associated with dislocations are, in general, larger than other precipitates, which are only a few nanometers in diameter. The size and distribution of the precipitates are consistent with the behavior previously suggested for all metals in silicon containing nanocavities—metal trapped in excess of the amount required to saturate the dangling bonds of the nanocavity surface precipitates within the nanocavity. The precipitates observed in the samples containing either Au or Cu and dislocations are larger than those seen in the samples containing nanocavities and these metals, examples of which from the Au sample are shown in Fig. 2(b). They are grouped along dislocations, and the small, randomly distributed precipitates as observed in the Au and Cu samples with nanocavities were not apparent. They strongly resemble the precipitates associated with dislocations seen in the samples containing nanocavities. This suggests that these precipitates in the nanocavity-containing samples are not the result of nanocavities filling but are precipitates forming on dislocation gettering.

It should be noted that nanocavities can pin dislocations; hence nanocavities can be expected to coincide with dislocations, and indeed this was observed in plan view TEM micrographs. However, the frequency of nanocavities coinciding with dislocations was far less than the frequency at which precipitates were found on dislocations; hence it seems unlikely that the nanocavities with pinned



dislocations yield the observed collocation of precipitates and dislocations.

The experiments reported here have revealed that the three metals behave differently. Cu and Au, both group IB metals, behave in a similar manner, with randomly distributed precipitates indicating that these metals do indeed preferentially fill nanocavities. The difference between the two group IB metals is related to the fact that Cu has a stable silicide phase and consequently results in the formation of larger precipitates than would be the case if the Cu precipitated in a metallic phase. In contrast to Au and Cu, Pd exhibits a strong preference for precipitation on dislocations. Indeed, all the precipitates observed in samples containing Pd have been collocated with dislocations. We now present the following hypothesis to explain the gettering behavior of these metals on both nanocavities and dislocations, as well as predict the behavior of other metals.

Metals from group VIIIIB will be less effectively gettered than those from group IB (e.g., Cu and Au) as a result of several factors. Metals in group VIIIIB all have stable silicide phases while metals in group IB, with the exception of Cu, do not. Myers *et al.* have shown that atoms of group IB were bound as elemental metals in nanocavities, while metals in group VIIIIB were bound as silicide phases.<sup>17</sup> However, some elemental metal was found at the nanocavities, although at much lower levels than was observed for the group IB metals. This was explained by multivalent nature of the group VIIIIB metals, while the group IB metals are monovalent. Consequently, each atom of the group IB metals can be satisfied by bonding with one Si atom on the nanocavity surface, whereas each atom of the group VIIIIB metals requires multiple Si atoms to form a stable bond. Therefore, the group VIIIIB metals will saturate the nanocavity surfaces with much fewer atoms than the group IB metals.<sup>18</sup>

When the surfaces of the nanocavities are saturated with chemisorbed metal atoms, excess metal is driven to precipitate and the location of these precipitates depends on the metal's group. Metals in group IB, generally lacking a stable silicide phase, will form a mono-elemental phase. As the nanocavity surfaces are already lined with metal, excess metal will bond to metal atoms already present and consequently the nanocavities fill with metal. Metals in group VIIIIB are more stable in a silicide phase, and the dislocations formed alongside the nanocavities will be a favorable site for precipitation relative to bulk material. Other precipitation sites, such as nanocavity surfaces, the sample surface, or

implantation damage, will compete with these dislocations. The nanocavity surfaces do not appear to be favorable for the formation of group VIIIIB silicides, unlike the group IB silicide  $\text{Cu}_3\text{Si}$ , based on the precipitate distribution seen in plan view TEM. This is potentially due to insufficient metal on the nanocavity surface. As dislocations are collocated with nanocavities, it has not been evident in previous experiments that the excess metal was precipitating on dislocations.

In conclusion, previous studies have examined the trapping effect of a nanocavity structure as a whole, comprised of nanocavities and secondary defects formed during nanocavity formation. We have demonstrated that these defects have a significant role in the trapping of metals such as Pd. Dislocations do not appear to be preferential gettering sites for Au or Cu when nanocavities are present, in contrast with Pd where the excess metal is preferentially gettered to the dislocations.

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