

Annealing of Heavily Arsenic-Doped Silicon: Electrical Deactivation and a New Defect Complex

K. C. Pandey, A. Erbil,^(a) G. S. Cargill, III, and R. F. Boehme

IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598

and

David Vanderbilt

Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 6 November 1987)

Ab initio total-energy calculations indicate that the formation of a new defect complex, a vacancy surrounded by four arsenic atoms, is responsible for electrical deactivation and for structural changes seen in measurements of extended x-ray-absorption fine structure when heavily arsenic-doped silicon is annealed. The v -As₄ complex is energetically favored over both substitutional, isolated As in Si and substitutional Si-As₄ configurations, and it is neutral and electrically inactive. The formation of such defects may be a widespread occurrence in silicon and in other semiconductors.

PACS numbers: 61.70.Sk, 61.70.At, 72.80.Cw

Nonequilibrium processing for control of material composition and atomic-scale structure is often needed to obtain desired properties in very-large-scale integration applications. For example, silicon with high electrical conductivity is obtained by the incorporation of doping impurities in excess of equilibrium limits, using ion implantation and rapid annealing.¹ However, the technological usefulness of such very heavily doped Si:As has been limited, because its electrical conductivity is strongly decreased by subsequent heating to temperatures as low as 300°C.^{2,3} In the present work, first-principles total-energy calculations and extended x-ray-absorption fine-structure (EXAFS) measurements³ reveal the specific structural origin—vacancy-arsenic (v -As₄) complex formation—for electrical deactivation of heavily doped Si:As. In addition to the electrical deactivation, v -As₄ formation provides a simple and natural explanation for the clustering of As atoms on the next-nearest-neighbor sites shown by our EXAFS data. In our calculations we do not assume a prior existence of vacancies which become decorated by As, which would be analogous to As passivation of the Si(111) surface.^{4,5} Instead, we show that even after paying the energy cost of creating the vacancy, v -As₄ formation is favored over isolated, substitutional As atoms in Si; this is a particularly interesting case of exothermic vacancy formation. The arsenic environment for this v -As₄ complex is similar to that for As in the equilibrium crystalline compound AsSi.⁶ Further, we show that the detailed geometry of the v -As₄ complex derived from our calculations is consistent with Rutherford backscattering data^{3,7} for electrically inactive As in Si.

Previously, various arsenic clusters and arsenic-vacancy complexes had been proposed to explain deactivation of arsenic dopants in silicon,^{2,7-11} without either firm theoretical support or direct experimental evidence. However, the v -As₄ complex, coherent with the silicon

lattice, had not been considered, and energy calculations had been reported for none of the previously proposed complexes.

To show that formation of the v -As₄ complex is energetically favorable, relative to both isolated As dopants and Si-As₄ clustering, and leads to electrical deactivation, we have carried out extensive first-principles self-consistent total-energy calculations based on norm-conserving pseudopotentials in the repeated-cell geometry within the local-density formalism.^{12,13} This scheme is well proven and has recently been applied successfully to calculations on defects and diffusion.¹³ The calculations presented below are based on a supercell of 16 atoms (on an fcc lattice), which, though a small number compared to 54 used in a recent diffusion calculation,¹³ simulates the present physical problem much more realistically. Some of the calculations, discussed below, based on a larger cluster of 54 atoms with a lower As concentration, verify the conclusions derived from the 16-atom cluster. In order to maximize the accuracy of the relative energies of the different atomic configurations, all calculations have been carried out in exactly parallel fashion with use of a large number of sampling points (36) in the irreducible part of the Brillouin zone of the supercell and a relatively complete basis set of plane waves (energy cutoff of 11 Ry). All calculations are for neutral defects only.

Calculations have been carried out for both the ideal and the relaxed configurations. The latter were obtained by displacing all atoms in the cell until the Hellman-Feynman forces acting on them vanished. In Fig. 1, the energies for the ideal and the relaxed configurations are shown by the dashed and solid lines, respectively. The relaxation has the largest effect for the v -As₄ configuration. It has an energy 0.35 eV per As atom lower than that for isolated, substitutional As in Si, in both cases after relaxation. The imbedded Si-As₄ cluster has the

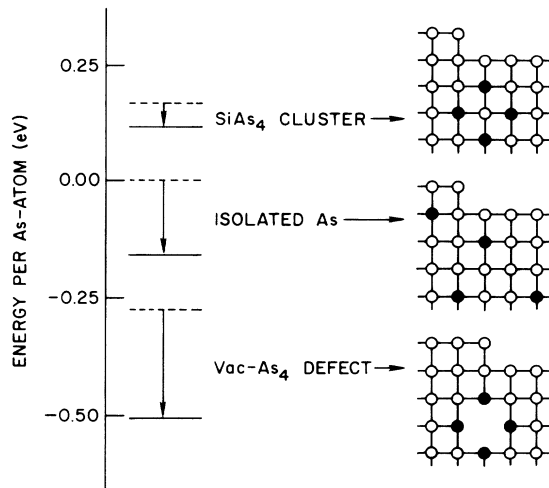


FIG. 1. Results of total-energy calculations for three different As-in-Si configurations. Energies per As atom are given for the ideal (unrelaxed) (dashed lines) and for the relaxed (solid lines) configurations. The energy for unrelaxed, isolated As in Si was set equal to zero.

highest energy, 0.27 eV per As atom greater than that for isolated, substitutional As in Si.

For the case of isolated, substitutional As in Si, the relaxed As-Si nearest-neighbor distance was 2.41 Å, or 0.06 Å greater than the usual Si-Si nearest-neighbor distance. This agrees with EXAFS results for 0.1, 0.7, and 7 at.% arsenic impurities in single-crystal silicon.¹⁴ For the v -As₄ complex, the As-Si bond length was accommodated with less overall strain of the lattice, since the four As atoms moved in toward the vacancy by 0.17 Å, and the average As-Si nearest-neighbor distance was 2.38 Å, or 0.03 Å greater than the usual Si-Si nearest-neighbor distance. This agrees with the average As-to-Si distance in crystalline AsSi, where each arsenic atom has only three nearest neighbors, all of which are silicon.⁶ It also agrees with the ~ 0.15 -Å displacement of As atoms deduced from channeling studies^{3,7} of thermally annealed, heavily doped Si:As. For the Si-As₄ complex the average As-Si nearest-neighbor distance was also 2.38 Å.

Calculations show that, irrespective of relaxation, both isolated As and Si-As₄ give rise to bands in the gap associated with hydrogenic donor levels. For the unrelaxed v -As₄ complex, the bands associated with the lone-pair orbitals overlap the valence band with no states in the gap. This band moves further into the valence band with relaxation. In the fully relaxed configuration, the maximum in the density of states lies approximately 0.5 eV below the valence-band maximum. This is similar to the effect of relaxation on the As-derived states on the GaAs(110) surface.¹² Thus, the neutral v -As₄ complex is electrically inactive.

Total-energy calculations were also made with a 54-atom supercell (energy cutoff of 11 Ry) for isolated, sub-

stitutional As in Si, without relaxation; and for the v -As₄ complex, taking relaxed coordinates from the 16-atom-supercell calculation and adding 38 additional silicon atoms on lattice sites. For this v -As₄ calculation, the concentration of arsenic was the same as for the actual Si:As samples. The energy per As atom from the 54-atom-supercell calculation for v -As₄ was only 0.04 eV lower than the corresponding result from the 16-atom-supercell calculation, whereas energies calculated for the three different arsenic environments differed by at least 0.35 eV. This confirms that the smaller supercell is adequate for these calculations.

Now we turn to the experimental support for formation of v -As₄ complexes. Previous experimental studies of structural changes accompanying initial stages of electrical deactivation in Si:As had been largely limited to ion-channeling measurements and electron microscopy.^{2,3,7} The present EXAFS measurements provide more detailed structural information about this process, using Si:As samples prepared by 100-keV ion implantation with 6×10^{16} As/cm² into [100] Si, followed by laser annealing with a frequency-doubled neodymium-doped yttrium-aluminum-garnet Q -switched laser.^{3,14} Sheet resistivity, alpha-particle channeling, and arsenic EXAFS measurements were made for samples in the as-laser-annealed condition and for samples subsequently furnace annealed for 30 min at temperatures between 200 and 800 °C. Some results from these measurements are shown in Fig. 2. Details of the EXAFS measurements and analysis are described in Ref. 14.

As expected,⁷ furnace annealing causes increases in electrical resistivity, because of the progressive electrical deactivation of the arsenic. Alpha-particle backscattering measurements indicate that the depth distribution of arsenic is not significantly broadened by the annealing, but channeling data show that As atoms are increasingly displaced from substitutional sites for higher annealing temperatures. Displacements of both As and Si atoms are particularly prominent for 700 and 800 °C anneals. Transmission electron microscopy and x-ray rocking-curve observations¹⁵ indicate that precipitation which heavily strains the silicon lattice occurs at 700 and 800 °C.

The model¹⁴ used to analyze the EXAFS measurements for nearest-neighbor (NN) surroundings of arsenic atoms fixed the As-As distance $r_{\text{AsAs}}^{\text{NN}}$ at 2.45 Å, and for next nearest neighbors (NNN) assumed that $r_{\text{AsAs}}^{\text{NNN}} = r_{\text{AsSi}}^{\text{NNN}} \equiv r^{\text{NNN}}$. The total numbers of nearest neighbors and of next nearest neighbors of arsenic atoms were assumed to be four and twelve, respectively. From this analysis, values determined for $r_{\text{AsSi}}^{\text{NN}}$ and for r^{NNN} remain unchanged by furnace annealing for all samples, within the uncertainty of these measurements. The As-to-Si NN distance is 0.06 ± 0.02 Å larger than the usual Si-to-Si NN distance, but the NNN distances are identical ± 0.02 Å.

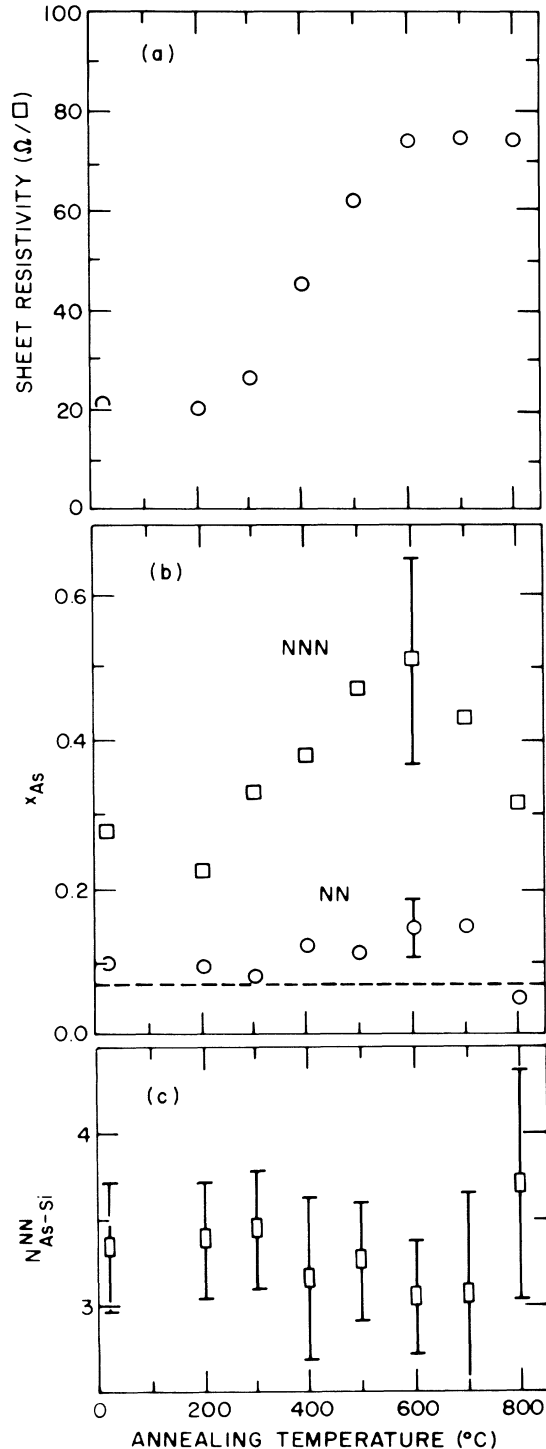


FIG. 2. (a) Sheet-resistivity measurements for Si:As samples, as-laser annealed, and after isochronal (30 min) furnace anneals at temperatures between 200 and 800 $^{\circ}\text{C}$. (b) Arsenic concentration x_{As} in nearest-neighbor (circles) and next-nearest-neighbor (squares) positions around other arsenic atoms for Si:As samples. The dashed line represents the value of x_{As} expected for a random solid solution. Error bars are discussed in the text. (c) Number of occupied nearest-neighbor lattice sites around arsenic atoms for Si:As samples, assuming that there are no As-As nearest-neighbor pairs.

The chemical compositions of the As NN and NNN environments, expressed in terms of $x_{\text{As}}^{\text{NN}} = N_{\text{AsAs}}^{\text{NN}}/4$ and $x_{\text{As}}^{\text{NNN}} = N_{\text{AsAs}}^{\text{NNN}}/12$, are shown in Fig. 2(b). $N_{\text{AsAs}}^{\text{NN}}$ is the average number of As nearest neighbors for As atoms, and $N_{\text{AsAs}}^{\text{NNN}}$ is the average number of As next nearest neighbors for As atoms. $x_{\text{As}}^{\text{NNN}}$ increases strongly with annealing temperatures up to 600 $^{\circ}\text{C}$, although $x_{\text{As}}^{\text{NN}}$ remains much closer to the value expected for a random solid solution. Error bars in Figs. 2(b) and 2(c) correspond to the range of values which increase the mean square fitting error by no more than 100%, as discussed in Ref. 14. As noted above, these results were obtained assuming the total coordination number $N_{\text{AsSi}} + N_{\text{AsAs}}$ to be fixed at 4 for nearest neighbors and at 12 for next nearest neighbors.

If vacancies (x_v), as well as As atoms (x_{As}) and Si atoms ($x_{\text{Si}} = 1 - x_v - x_{\text{As}}$), are considered, then both x_{As} and x_v cannot be determined independently from EXAFS data for NN sites around As atoms. For the results shown in Fig. 2(b), it was assumed that $x_v^{\text{NN}} = 0$. However, if instead it is assumed that $x_{\text{As}}^{\text{NN}} = 0$, i.e., no As-As nearest neighbors, analysis of the EXAFS data gives the values of $N_{\text{AsSi}} = 4 - N_{\text{Asv}}$ shown in Fig. 2(c). Just as the data of Fig. 2(b) suggested a slight increase in $x_{\text{As}}^{\text{NN}}$ with increasing annealing temperatures to 600 $^{\circ}\text{C}$, the data of Fig. 2(c) suggest a decrease of N_{AsSi} (increase of N_{Asv}) with increasing annealing temperatures to 600 $^{\circ}\text{C}$, which is the interpretation supported by the total-energy calculations. Also, slightly smaller $r_{\text{AsSi}}^{\text{NN}}$ distances, 2.38 \AA , are obtained in this case, which agree with those calculated for $v\text{-As}_4$ complexes. In fact, annealing may both decrease the number of As-As nearest neighbors and increase the number of As-vacancy pairs. The actual changes in N_{AsSi} would then be greater than those shown in Fig. 2(c). In any case, the error bars are too large for more definite conclusions to be drawn from these data.

Analysis of the EXAFS experiments shows that even the as-laser-annealed Si:As contains an excess of As-As NNN's, and that this excess grows for annealing treatments for $T \leq 600$ $^{\circ}\text{C}$. An increase in the number of As-As second nearest neighbors, without a corresponding increase in the number of As-As nearest neighbors, requires both clustering and ordering of the arsenic in silicon. These results are consistent with formation of $v\text{-As}_4$ complexes coherent with the silicon lattice.

These new theoretical and experimental results provide strong evidence for the role of $v\text{-As}_4$ arrangements coherent with the silicon lattice as the energetically favored and actually occurring complexes responsible for the initial stages of electrical deactivation in heavily doped Si:As. On simple chemical considerations, we expect that the formation of analogous defects might also occur in other group-IV semiconductors doped not only with group-V but also with group-III elements. We believe that larger defect clusters, e.g., $v_2\text{-As}_6$, should also form on annealing and that $v\text{-As}_4$ is only the first step in

the eventual precipitation of As. In this paper we have not considered the energetics of other, precursor defects $v\text{-AsSi}_3$, $v\text{-As}_2\text{Si}_2$, and $v\text{-As}_3\text{Si}$; this would be an interesting problem for further study.

We thank P. Saunders for help with backscattering measurements and the staff of the Cornell High Energy Synchrotron Source for assistance with EXAFS measurements. David Vanderbilt acknowledges work support from National Science Foundation Grant No. DMR-85-14638. Work by A. Erbil at Georgia Tech was supported by an Alfred Sloan Fellowship and an IBM Faculty Development Award.

^(a)Present address: School of Physics, Georgia Institute of Technology, Atlanta, GA 30332.

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