

**BEAMLINE**  
X15B

**PUBLICATION**

P. M. Voyles, D. A. Muller, J. L. Grazul, P. H. Citrin, and H.-J. L. Gossmann, "Atomic-scale Imaging of Individual Dopant Atoms and Clusters in Highly n-type Si", *Nature* **416**, 826 (2002).

**FUNDING**

Lucent Technologies

**FOR MORE INFORMATION**

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## Imaging Single Dopant Atoms and Clusters in Bulk Silicon

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*As silicon-based transistors in integrated circuits grow smaller, the concentration of charge carriers generated by impurity dopant atoms must steadily increase to maintain the transistors' performance. But current technology is rapidly approaching the limit at which introducing additional dopant atoms ceases to generate additional charge carriers, because the dopants form electrically inactive clusters. Scientists from Bell Laboratories have used x-ray absorption measurements at beam line X15B of the National Synchrotron Light Source, and scanning transmission electron microscopy (STEM) to understand the nature of these dopant clusters in silicon. The STEM data represent the first observation of single atoms and clusters the size of a few billionths of a meter inside a bulk solid, and they provide insight into how the clusters are formed.*

The electrical properties of a semiconductor – a material having electrical conductivity greater than insulators but less than good conductors, and used especially as a base material for computer chips and other electronic devices – can be controlled by adding small amounts of foreign atoms, called dopants. When dopants such as antimony are added to a semiconductor such as silicon, the dopants occupy lattice sites (the locations occupied by atoms in the crystal) in place of silicon atoms, and donate electrons, thus changing the electrical properties of the silicon.

The shrinking size of electronic devices requires that the concentration of electrons – and therefore the concentration of dopants needed to generate them – must increase to maintain device performance. However, at the high dopant concentrations needed for future silicon device technology, not all the

dopants remain electrically active. Instead, they form electrically inactive clusters. It is therefore important to understand how the dopant atoms become electrically inactive, leading to the observed saturation of free-electron densities.

We have shown, by performing extended x-ray absorption fine structure (EXAFS) measurements at beamline X15B that, in highly antimony-doped silicon samples, the most commonly accepted models for the dopant clusters, in which

three or four antimony atoms surround a silicon vacancy, were not correct. We used first-principles calculations, which suggest that the dominant clusters in these samples contain only two dopant atoms with no silicon vacancies.

These findings have now been tested using scanning transmission electron microscopy (STEM) on the same antimony-doped samples after mechanically thinning them to a thickness of less than five nanometers. (One nanometer is one billionth of a meter.) The thinning procedure was particularly demanding, because surface roughness and oxidation had to be kept to a minimum to ensure maximum imaging contrast between the crystalline silicon and antimony atoms. The small sample thickness was important for optimizing the likelihood that only a single antimony atom would occupy a given column of silicon atoms when viewed in projection.



Authors of the study (from left to right): David Muller, Paul Citrin (seated), Hans Gossmann, John Grazul, and Paul Voyles (lead author).

**Figure 1** shows a STEM image of a sample. The atomic columns of silicon containing at least one antimony atom are seen as the brightest dots on the left, whereas no such dots are seen in the undoped region on the right. Applying filtering and particle-counting algorithms to such images from samples only 2.3 and 1.5 nanometer-thick (corresponding to 11 and 9 silicon atoms per column) revealed that the distribution of single dopant atoms was purely random. This suggests that overcoming free-electron density saturation at

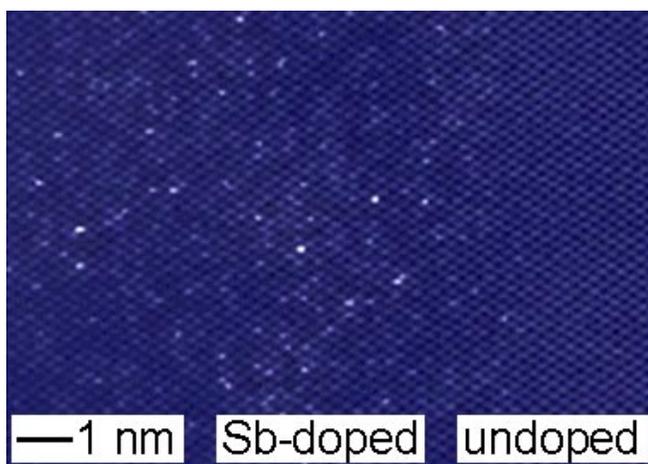
very high dopant concentrations will be a major challenge.

**Figure 2** compares calculated structures for clusters containing two and three antimony atoms with corresponding simulated and experimental images. Careful analysis shows that the two-atom clusters outnumber those with three or four atoms by 50:1.

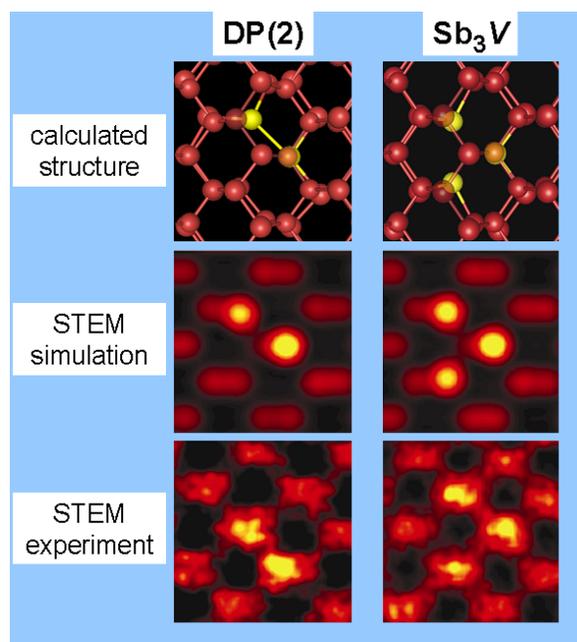
The observed random distribution of dopants provides insight into the formation mechanism of the clusters. We have recently performed

additional experiments and calculations to characterize the two-atom structures more completely, and the results are being prepared for publication.

Our study provides the first, unambiguous observation of single dopant atoms within a bulk crystal. This observation paves the way for further analysis of single atoms and clusters of two to four atoms, and for the study of the structure of impurities and alloy constituents in crystalline solids.



**Figure 1.** Scanning transmission electron microscopy image of a cross-section of highly antimony-doped silicon. The brightest dots (left) are atomic columns of one or more antimony atoms, which are absent in the undoped sample (right).



**Figure 2.** Calculated structures compared with simulated and experimental scanning transmission electron microscopy images of a donor-pair defect cluster with 2 antimony dopant atoms and no silicon-atom vacancy (left) and of a 3-antimony-atom cluster surrounding a vacancy (right). Antimony and silicon atoms are in yellow and red, respectively. The silicon atoms appear orange when in front of antimony atoms.