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Static charge fluctuations in Ga^+-implanted silicon

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The peak width of the Si 2*p* core level (measured by photoemission spectroscopy) is found to vary with substitutional Ga concentration. This is attributed to static charge fluctuations brought about by bond-length and bond-angle deviations induced by Ga atoms. In crystalline materials, the estimated mean charge fluctuation ranges from 0.04 to 0.003 electrons, depending upon Ga concentration. For the unreconstructed Si lattice, a large charge fluctuation, of 0.11 electrons, is found, and explained as due to the amorphous nature of the Ga^+-implanted layer.

Based on calculations of random-network models of amorphous silicon (*a*-Si), Guttman, Ching, and Rath[1] have proposed that there exist fluctuation of the net atomic charge of about 0.2 electrons rms on an *a*-Si cluster as a result of the deviations of bond length and bond angle from their values in the crystal. As dopant atoms generally have radii different from that of Si atoms, they can cause the silicon lattice to expand or contract, following Vegard's law.[2,3] From extended x-ray absorption fine-structure measurements, Erbil *et al.*[4] have shown that As to Si nearest-neighbor and next-nearest-neighbor distances are 2.41 and 3.85 Å, respectively. This yields an As–Si–Si bond angle of 106.0°, which deviates by 3.5° from the ideal Si–Si–Si bond angle of 109.5°. This deviation is comparable to the average bond-angle deviation of about 7° in an *a*-Si continuous random network.[5] Dopant-induced static charge fluctuations should, therefore, produce effects comparable to those in amorphous Si at sufficiently high doping levels. In a previous work,[6] we reported that static charge fluctuations in the Si valence shell brought about by substitutional Ga lead to a broadening in the core-level photoelectron spectra, as they do in *a*-Si (Ref. 7) and Si oxides.[8] In this paper, we present a quantitative estimation of the static charge fluctuations induced by the substitutional Ga.

Supersaturated substitutional Ga in Si was obtained[6] by low-energy (4 keV) ion implantation and rapid thermal annealing. The Ga atoms, as high as 10 at.%, were found to occupy substitutional sites in the recrystallized material, as indicated by x-ray photoelectron spectroscopy (XPS) measurements, which were carried out on a VG ESCALAB MKII system. The sampling depth of XPS by Mg $K\alpha$ radiation (1253.6 eV) is about 50 Å, which principally reflects the bulk structural property of the material analyzed.[9]

In Fig. 1, we show typical Si 2*p* core-level spectra obtained from unimplanted, and from Ga^+-implanted and annealed crystalline silicon (*c*-Si). The experimental data (shown as filled circles) were curve resolved by least-squares curve-fit methods. The input parameters for all spectra were held constant except for the full width at half maximum (FWHM), as reported elsewhere.[6] The doublet shown in the figure for unimplanted *c*-Si, is due to the spin-orbit splitting of the *L* shell (or 2*p* core level). In Ga^+-implanted and annealed *c*-Si, two doublets were deconvoluted. One is at the same energy as that for unimplanted *c*-Si, and corresponds to Si atoms bonded to four other Si atoms. The other, with a chemical shift of 0.6 eV to lower binding energy, corresponds to Si atoms bonded to three other Si atoms, and to one tetrahedrally coordinated Ga atom.[6] In Table I, we give the Si 2*p* peak width or FWHM as a function of Ga concentrations (with annealing temperature as a parameter). In Table I, we show the mean static charge fluctuations on silicon atoms, estimated by a method presented below.

The peak width of a core level is known to consist of a

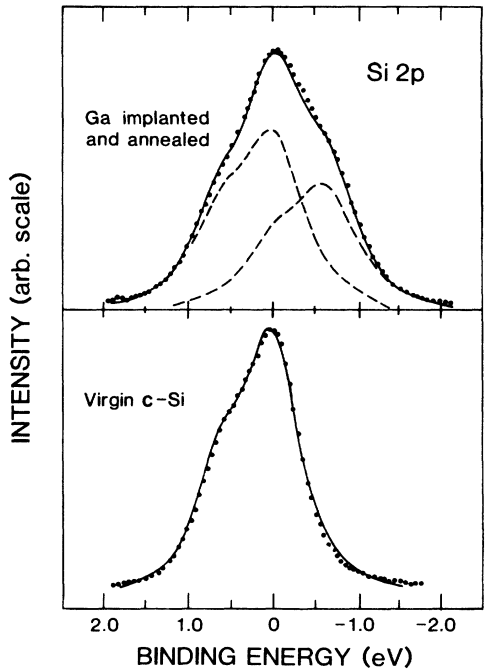

FIG. 1. Si 2*p* core-electron spectra of virgin, and Ga^+-implanted and annealed *c*-Si. The data points are shown by dots. A fit to a single spin-orbit pair for the virgin *c*-Si sample is shown by the solid curve. For the Ga^+-implanted and annealed sample, the dashed curves show the results of least-square fits of bulk Si and chemically shifted components and the solid curve is the sum of the components. Intensities are shown on an arbitrary scale and binding energies are aligned to a Si $2p_{3/2}$ level of 99.6 eV.

TABLE I. Calculated static charge fluctuations in Ga^+-implanted Si as a function of annealing temperature T_a.

T_a (°C)	FWHM (eV)	Ga/Si (at.%)	$\langle \Delta q \rangle$ ($\lvert e - \rvert$)
300	1.00		0.11
400	1.00		0.11
500	0.80	10	0.04
600	0.75	9	0.02
800	0.72	4.5	0.003
900	0.70	0	
Virgin Si(100)	0.70		

convolution of (a) the width of the photon source, (b) the resolution of the electron energy analyzer, and (c) the natural or inherent width of the core level. If spectra are taken under identical instrument conditions, contributions (a) and (b) should not change. The natural linewidth of the core electron is governed solely by the lifetime of the core hole that must be created in the photoemission process. In the case of silicon, the lifetime of the L shell (or $2p$ level) holes are dominated by the Auger process,[10] and varies slightly for elements with atomic number from $Z=10$ to 25. There is no strong experimental or theoretical evidence that these lifetimes are affected by valence shell charge transfer.[9,10]

Experimentally, it is found[11] that the chemical shift ΔE of inner core levels is proportional to the valence shell charge transfer Δq, that is, $\Delta E = \beta \Delta q$. The proportionality constant β has a value of approximately 2.2 eV per electron for the Si $2p$ level, as deduced from chemical shift data on SiO_x.[12] In what follows, we represent the Si $2p_{3/2}$ peak by a convolution function $f(E,\zeta)$, where E is the binding energy (99.6 eV) and ζ is the FWHM providing the best fit to the experiment data. Measurements on unimplanted c-Si yield a FWHM of $\zeta = \zeta_0 = 0.7$ eV. If the Si valence charge deviates by Δq_i from the ideal charge of four electrons, the corresponding core levels should have a chemical shift of $\Delta E_i = 2.2 \Delta q_i$. So the broad peak $f(E,\zeta)$ observed may be interpreted as the sum of the unshifted peak $f(E,\zeta_0)$ and the shifted peaks $f(E+\Delta E_i,\zeta_0)$. This can be written as

$$f(E,\zeta) = B f(E,\zeta_0) + \sum_i C_i f(E+\Delta E_i,\zeta_0) ,$$

where B and C_i are normalized peak intensities, which directly represent the percentage of Si atoms with ideal charge of four electrons, and the percentage of Si atoms with net charge deviation Δq_i. As an approximation, we may rewrite the above equation as

$$f(E,\zeta) \approx B f(E,\zeta_0) + C f(E+\Delta\varepsilon,\zeta_0) + C f(E-\Delta\varepsilon,\zeta_0) ,$$

where $\Delta\varepsilon$ represents the absolute value of the average chemical shift brought about by a net average charge fluctuation of Δq. The use of the same peak intensity C in the last two terms on the right-hand side of the above equation represents the observed symmetric broadening in the $2p$ core-level spectra. Parameters B, C, and $\Delta\varepsilon$ can be determined by a least-squares fit of the sum of the three terms on the right-hand side to the term on the left-hand side of the equation, for each observed ζ. The mean net static charge fluctuation $\langle \Delta q \rangle$ per Si atoms is then estimated to be $\langle \Delta q \rangle = 2C\Delta\varepsilon/2.2B$. This is shown in the last column of Table I.

From Table I we see that a large FWHM value of 1.0 eV for samples annealed at temperatures $\leq 400\,^\circ$C yields a mean static charge fluctuation of 0.11 electrons. The same value for $\langle \Delta q \rangle$ in sputtered a-Si was reported by Ley *et al.*[7] using a different method of estimation. A value for $\langle \Delta q \rangle$ of 0.2 electrons on atoms of an amorphous silicon cluster was calculated by Guttman *et al.*,[1] as discussed above. This suggests that static charge fluctuations in these samples are due to an unreconstructed Ga^+-ion amorphized Si lattice, in good agreement with photoemission valence-band density of states and low-energy electron diffraction (LEED) results.[6]

For samples annealed at temperatures $\geq 500\,^\circ$C, LEED suggests[6] that the Si lattice has completely reconstructed, leaving no amorphous (as expected from the work of Donovan *et al.*[13]) or polycrystalline residue. A significant amount of Ga has been promoted to substitutional sites. $\langle \Delta q \rangle$ ranges from 0.04 to 0.003 electrons, depending upon the amount of substitutional Ga in the lattice. The static charge fluctuations in these samples may be explained as largely due to substitutional Ga. This is understandable. As the Si–Ga bond length (2.398 Å) is larger than that of the Si–Si bond (2.346 Å)[14] in pure silicon, the substitutional Ga will induce bond-angle and bond-length deviations in the first, second, or further neighbor Si–Si bonds, as we have discussed in the case of substitutional As in Si. Consequently, the bond-angle and bond-length deviations will lead to Si valence shell charge distribution fluctuations as indicated by the calculation.[1]

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