Chemical information in positron annihilation spectra

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Positron annihilation spectra of arsenic- and gold-implanted silicon are compared with spectra from bulk samples of arsenic and gold. Spectra with strongly reduced background intensities were recorded using a two detector coincidence system with a variable-energy positron beam. It is shown that features in the high-momentum region of the spectra (∼514–520 keV) can be identified with particular elements and that this identification is independent of structure, i.e., whether the element forms the bulk or is an implanted impurity. Proportionality between the intensity of characteristic spectral features and the fraction of annihilating positrons is also demonstrated, using the native oxide on a silicon wafer as a test case. © *1996 American Institute of Physics.*
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During the last few decades, positron annihilation spectroscopy has been developed into a powerful and versatile tool in materials analysis. Recently,[1–5] two-detector coincidence arrangements[6] have been used to reduce experimental background, which allows analysis of higher-momentum components of the annihilation γ-ray spectra. Since the higher momentum components correspond to annihilation with electrons which are bound to atoms, they can be used to identify chemical species which surround the annihilation site. This may greatly enhance the capability of the positron technique to identify impurity-defect complexes in semiconductors. The method has been used, for example, to characterize the annihilation site in InP and in GaAs.[1] Recent work on As-doped silicon[3] showed that electrically inactive As was complexed with vacancies at the annihilation site. Spectral features identified with As in silicon were identified by their similarity to features in the spectrum of bulk As. Sb in silicon has been similarly identified.[5] Calculation of the annihilation line shapes for several bulk elements[2] shows good agreement with experimental spectra. In this contribution we show evidence to support the validity of these elemental identifications, by making comparisons between spectra obtained from bulk elements and the corresponding ions implanted in silicon.

Positrons are implanted into a sample material where they thermalize rapidly (∼10 ps) before annihilating with an electron, creating two γ quanta with energies of about 511 keV, emitted in close to opposite directions. The γ rays are Doppler shifted from 511 keV due to the motion of the electron, so the annihilation peak carries information about the electron momentum distribution. This is commonly used to identify vacancy-type defects in crystalline materials, which provide an attractive potential well for the positron. Because the probability of annihilation with valence electrons (compared with core electrons) is greater for positrons trapped by vacancies, the average momentum of the annihilating electrons is lower and a narrower annihilation line results. The linewidth is usually characterized by a parameter S, defined as the number of counts in a central region of the peak divided by total counts in the peak.

Conventional annihilation spectra have a peak to background ratio of about 250, obscuring the annihilation spectrum outside an energy range of 507–515 keV. Events due to annihilation with bound electrons lie outside this range but have a low count rate. On the low-energy side of the annihilation peak, the background problem is insurmountable due to incomplete charge collection in the detector. However, on the high-energy side of the peak it is possible to achieve high peak-to-background ratios by reducing pulse pileup (by using a moderate count rate) and suppressing other background sources by coincidence techniques.

To apply the two-detector coincidence technique, another detector is added collinearly with the first at the opposite side of the sample, and events are accepted only if a pulse is received from both detectors. Since good energy resolution is not required for the second detector, a NaI scintillator is used. We achieve a peak to background ratio of $\sim 10^5$ on the high energy side of the peak.

Measurements were carried out at the variable energy positron beam facility at the University of Western Ontario.[8] In a vacuum of about 10^{-7} Torr, monoenergetic positrons with energies between 0.5 and 60 keV are implanted into the sample. The primary detector is a 2×10 cm^3 HPGe detector with a resolution of about 1.3 keV at 511 keV. The auxiliary detector supplying the coincidence signals is a cylindrical 5 in.× 5 in. NaI(T1) scintillator with photomultiplier. The two detectors face each other at right angles to the direction of the incident positron beam. In this configuration, a coincidence rate of about 120/s is obtained (compared to a single detector rate of ∼3000/s). Coincidence spectra with $\sim 10^7$ counts in the peak were acquired, over a period of about 24 h. A simple smoothing routine (averaging over a number of channels) was applied and then the spectra were normalized to 10^5 counts in the central channel.

To emphasize differences between samples, we calculate quotient spectra by dividing the number of counts in each channel by the number of counts in the corresponding channel of a ''standard spectrum,'' obtained from a bulk silicon sample (Cz type, P doped, 1–1.7 Ω cm) using a beam energy of 40 keV. Annihilation peaks taken from samples of various elements exhibit considerably different shapes,[6,7] due to differences in the electronic shell structures of the elements. We show that the annihilation peak shape, as determined by us-

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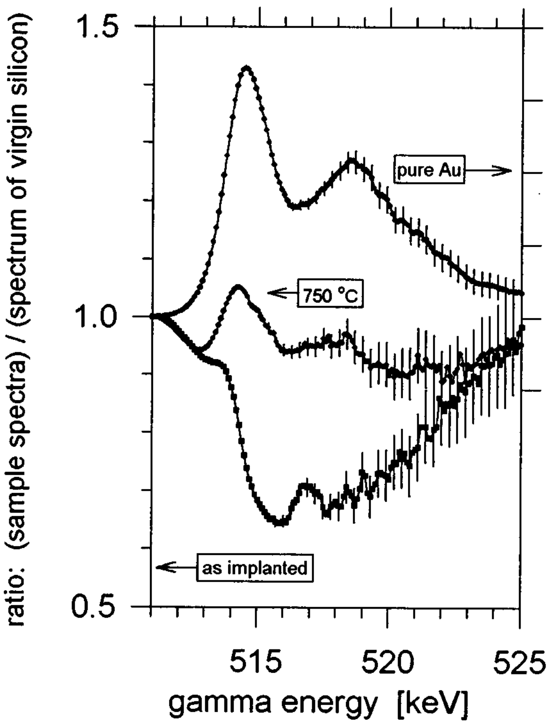

FIG. 1. Quotient spectra for a silicon sample implanted with 10^{14} cm^{-2} 3 MeV gold ions, before and after annealing at 750 °C. Positron energy was 10 keV. For comparison, the quotient spectrum for pure gold (taken at 40 keV) is also shown; for this spectrum the right intensity axis applies.

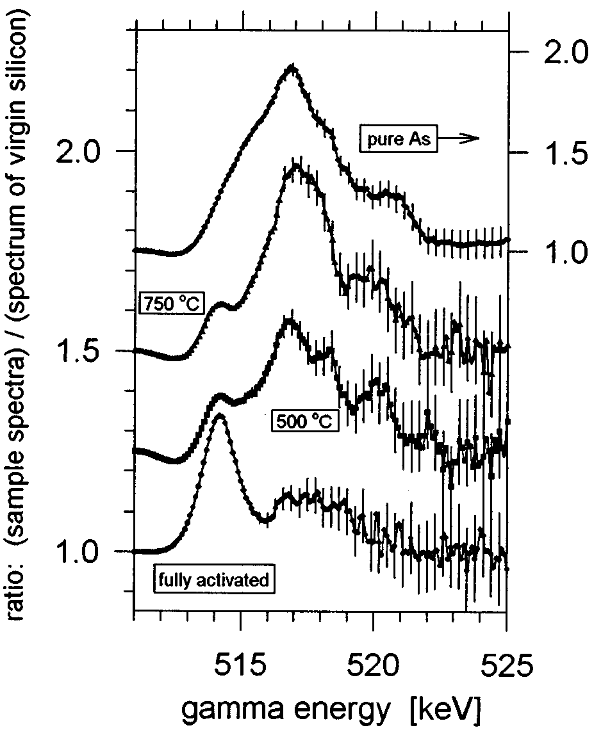

FIG. 2. Quotient spectra for arsenic implanted and laser activated silicon before and after heating to 500 and 750 °C. The positron energy was 12 keV. Spectra are offset by 0.25 each. For the quotient spectrum of elemental arsenic (taken at 40 keV) the intensity scale on the right applies.

ing a sample of the pure element, is conserved when this element is implanted into a silicon substrate, and therefore can be taken as a ''fingerprint'' characteristic of the element.

An example is gold. Fig. 1 shows the quotient spectrum of pure gold (i.e., the spectrum of gold divided by the standard spectrum of silicon). Dominant features are two peaks at 514.5 and 518.7 keV. Also shown are quotient spectra obtained from a silicon substrate implanted with 3 MeV gold ions to a fluence of 10^{14} cm^{-2}. The ion range, as predicted by TRIM simulations,[9] was 8000 Å. A positron energy of 10 keV was used, resulting in a mean penetration depth of about 7000 Å, i.e., in the implanted layer. Spectra were also obtained from this sample following annealing at 750 °C for 30 s. The spectrum taken directly after implantation shows values less than 1 for all energies, corresponding to an overall narrowing of the annihilation peak. In conventional positron spectroscopy, this result corresponds to a significant increase in the *S* parameter, due to the creation of vacancy-type defects along the tracks of the implanted ions. No gold signal is present in the''as-implanted'' spectrum, because the implanted gold atoms are not localized at the vacancies. Annealing the sample at 750 °C for 30 s greatly reduces the vacancy concentration. The appearance of peaks in the quotient spectrum corresponding to those in the spectrum of the pure gold sample suggests that the implanted gold atoms form complexes with the remaining vacancies. If the implanted gold was not attached to vacancies to form a positron trap, we would not expect to see a gold signal in the spectrum.

The detection of impurity-vacancy complexes of this kind is also possible in arsenic-implanted silicon. Figure 2 shows the quotient spectrum of pure arsenic, which exhibits a broad peak centered at 516.9 keV. Also shown are spectra from a silicon sample containing a 2000 Å thick arsenic-implanted layer with a concentration of 4×10^{20} cm^{-3}, fully activated by a laser melt anneal, and subsequently heated for 15 s to 500 and 750 °C. The main feature in the spectrum of the fully activated sample is a peak at 514 keV, due to the surface oxide layer (SiO_2 is discussed in detail below). In the region around 517 keV, where the arsenic signal has its maximum, only a small intensity is observed. Heating to 500 °C results in a peak similar to the pure arsenic peak. Heating to 750 °C increases the intensity of this peak. Recently, we reported the generation of a high concentration (about 2×10^{20} cm^{-3}) of vacancies associated with this thermal treatment.[10] Therefore in the two annealed samples the positrons most probably are trapped and annihilate within vacancies generated by the thermal treatment. The arsenic-related peak indicates the presence of arsenic atoms in the immediate vicinity of the vacancies, very likely forming $As_nSi_{4-n}-V_{ac}$ complexes as proposed in previous studies.[10,11] Due to trapping by vacancies, positron diffusion to the surface is strongly reduced, and only the very few positrons directly deposited into the surface oxide layer contribute to the oxide peak. This explains why the increase of the arsenic peak is accompanied by a decrease of the oxygen-related peak.

To date it has not been possible to predict theoretically the height of the peaks in the quotient spectra, and thereby determine for example, how many impurity atoms are involved in an impurity-vacancy complex. However it is possible to extract some quantitative information from the peak

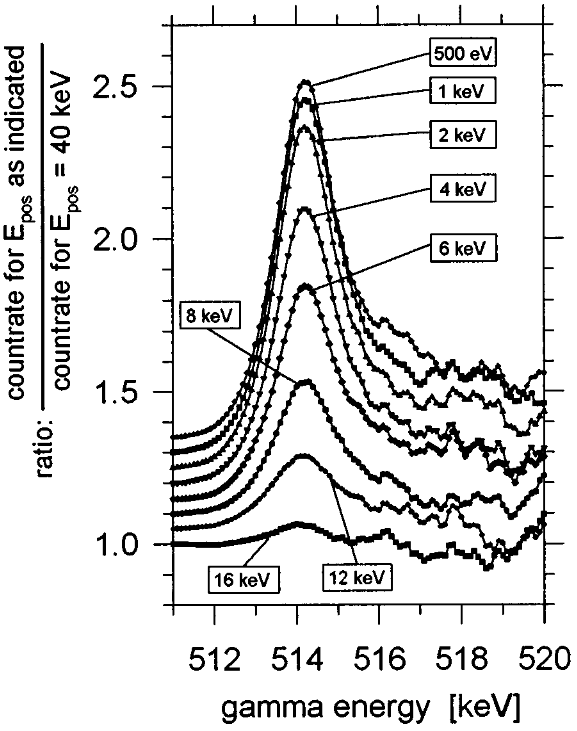

FIG. 3. Quotient spectra for a virgin silicon wafer. The measured spectra are divided by a spectrum taken on the same sample with a positron energy of 40 keV. For clarity, the quotient spectra are shifted by 0.05 each and error bars are omitted. The peak at 514.2 keV is due to a layer of native surface oxide.

heights. Because the spectra consist of linear superpositions of spectra from each of the possible annihilation states (i.e., bulk, trapped by defects, trapped in the surface oxide, etc.) it follows that the peak heights in quotient spectra are directly proportional to the fraction of positrons annihilating from a given state. We demonstrate this experimentally for the case of the native oxide layer on our ''standard'' silicon wafer. Spectra from this sample were recorded using various positron energies between 500 eV and 16 keV, and quotient spectra were calculated by dividing each of these by the ''standard'' spectrum taken at 40 keV. The resulting quotient spectra are shown in Fig. 3. All exhibit a peak at 514.2 keV, as do measurements of a pure SiO_2 sample (not shown). As the positron implantation energy is increased, the fraction of positrons implanted within a diffusion length of the surface decreases, and so does the height of the oxygen-related peak in the spectrum.

The fraction of positrons which annihilate at the sample surface can be determined by application of the standard (single detector) variable-energy positron annihilation spectroscopy. To this purpose, the $S(E)$ curve was measured in the single detector geometry and analyzed by deconvoluting the positron implantation distribution and diffusion using the program POSTRAP5.[12] This yields the fraction of positrons annihilating at the sample surface as a function of positron energy, shown as a continuous curve in Fig. 4. Discrete points in this figure represent peak intensities of the quotient spectra from Fig. 3. They are derived by subtracting 1 (since pure silicon gives an intensity of 1) from every peak value, and normalizing the results to 1 for the 500 eV spectrum (for which virtually all positrons diffuse to the surface). Clearly, these points agree well with the theoretical curve, which also fits the measured S vs E data (not shown).

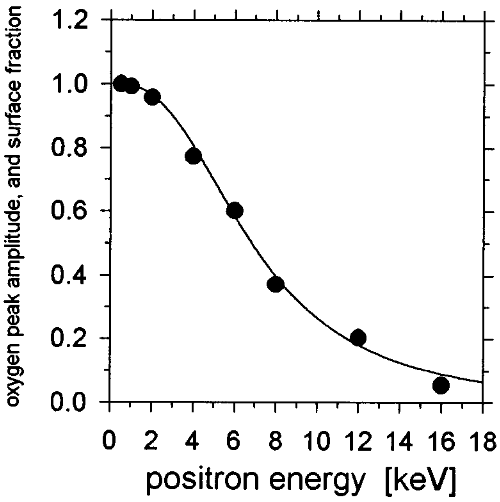

FIG. 4. Measured intensity of the surface oxygen peak at 514.2 keV (points) and fraction of positrons annihilating at the sample surface as predicted by POSTRAP5 (continuous curve) as a function of positron energy. The experimental error lies within the data point diameter.

In summary, we have shown that implanted impurities in silicon produce peaks in positron annihilation quotient spectra which are characteristic ''fingerprints'' of the elemental species. This result is perhaps surprising since one would expect the detailed shape of the annihilation spectrum to be dependent on the structure and microscopic arrangement of atoms surrounding the annihilation site.

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