ADVANCES IN DEFECT CHARACTERIZATION OF SEMICONDUCTORS USING POSITRONS

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Positron Annihilation Spectroscopy (PAS) is a sensitive probe for studying the electronic structure of defects in solids. We summarize recent developments in defect characterization of semiconductors using depth-resolved PAS. The progress achieved in extending the capabilities of the PAS method is also described.

1. Introduction

The understanding of defects and controlling their production and evolution have been a subject of immense interest to the semiconductor community. With the advances in the growth techniques, we have seen a corresponding progress in their characterization techniques. Often, the drawback of relying on a handful of characterization techniques, however well-tested they might be, has become apparent. Therefore, various communities are ever seeking the refinement of the existing probes and development of newer techniques. In this regard, the Positron Annihilation Spectroscopy (PAS) is emerging as a powerful tool to detect and characterize low concentrations of open-volume defects. Recent advances in PAS - some of them described below - allow to gather unique quantitative information that is either difficult or impossible to obtain with other techniques, yet are shown to be important to the development of advanced structures and devices.

The PAS technique relies on the information contained in the ~ 511 keV photons emerging from the annihilation of positrons and electrons. When positrons are introduced into a solid, they seek out low-density regions such as voids and vacancies. The localized positrons annihilate with characteristics that are clearly distinct from the freely diffusing positrons. Due to the penetrating nature of the annihilation gamma rays, these signatures escape the test system without significant attenuation, and allow the experimenters to derive unique information about the electron densities and electron momentum distributions around the annihilation site. Besides the superb sensitivity of the technique in detecting low concentration of open-volume defects, the technique also is depth-resolving (from nm to μm ranges), non-contact, and nondestructive.

This article summarizes some of the recent developments in the PAS field. The topics are selected to show the trends in the field rather than providing an exhaustive review, owing to the nature of the paper.

2. Experimental Method

The most often used positron observables for defect characterization in semiconductors are the

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lifetime, Doppler Broadening of the Annihilation Spectrum (DBAS), and Two-Dimensional Angular Correlation of the Annihilation Radiation (2D-ACAR)[1,2]. With the advances in the positron beam technique, last decade saw an increase in the number of positron facilities characterizing the defects in the near-surface region and at the interfaces of semiconductor systems. Some of the advances using a pulsed positron beam for lifetime studies will be covered by other articles in these proceedings. We will concentrate on the DBAS and 2D-ACAR results in semiconductors.

The DBAS arises from the Doppler shift of the annihilation gamma rays, caused by the center-of-mass motion of the electron-positron system. Since the positrons are thermalized before annihilation, the Doppler shift is dominated by the electron momentum. Traditionally the central region of the Doppler

Figure 1. Comparison of the Doppler-broadened annihilation spectrum of bulk crystalline Si using the traditional single Ge detector setup and the improved two-detector coincidence system.

spectrum is characterized using a shape parameter known as S-parameter. The S-parameter is defined as the number of counts recorded in a central window (~ 1.5 keV wide) to the total counts of the DBAS. The S parameter is higher at open-volume defects compared to a "defect-free" material. The S-parameter measurements as a function of depth can be used to profile defects in the near surface region of a semiconducting material[3].

A new feature emerging in PAS is the elemental specificity of the DBAS. The S-parameter is sensitive to events with no or small Doppler shifts, and arises mainly from low-momentum electrons. The high-momentum electrons produce large Doppler shifts. Therefore, the tail regions of the DBAS arise mostly from inner-shell electrons, with a small part arising from high momentum components of the valence electrons. The inner-shell

electrons retain their atomistic character even in a solid. Therefore, the shape variations in the tail region of the DBAS arising from different elements can be used to chemically "fingerprint" them. However, in a standard Doppler measurement system, the tail region is dominated by background events arising due to pileup, sum, incomplete charge collection, three photon annihilation of positrons, and Compton events in the detector window material. The high background and the low probability of the positron annihilation with inner shell electrons make it difficult or impossible to examine the shape variations using the standard single

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detector setup, without complicated background subtraction procedures.

A coincidence system that detects the energies of both gamma rays - one upshifted and other down shifted from the center energy of 511 keV - from an annihilation event can nearly eliminate the background contribution to the tail region of the DBAS[4]. Fig. 1 shows the improvements obtained with the coincidence system. While the traditional single detector setup can attain a peak to background ratio of only ~ 200 , the new setup attains a peak to background ratio of 10^5 . The tail region is elemental specific as demonstrated in Ref. 4. The elemental specificity of the DBAS can be used to study impurity-vacancy complexes, vacancies in the different sublattices of a compound semiconductor, and impurity-decorated internal and external surfaces.

The 2D-ACAR measurements provide detailed information regarding the momentum distribution of the annihilating positron-electron pair by measuring the angle between the two gamma rays. The conventional 2D-ACAR measurements use radioisotopes as the source of positrons. As a result, positrons of wide energy distribution will enter the material under study, making the study of interfaces and thin films difficult. Since the high resolution 2D-ACAR measurements force the two detector arrays to be kept far apart, the depth-resolved measurements have been difficult due to the low positron intensity. Recently, this has been remedied with the development of intense positron beams[5].

3. Results and Discussion

As stated above the tail region of the DBAS spectrum contain information specific to the high momentum core electrons. As shown in Fig. 1, the DBAS spectrum spans several orders of magnitude. Therefore, the shape variations are better seen by normalizing the spectrum to a reference element. The reference spectrum is obtained using a Float-Zone, high resistivity Si (100) wafer with a positron incident energy of 50 keV. At 50 keV, the positrons penetrate to a mean depth of $\sim 9 \mu\text{m}$, deep enough to exclude ($<1\%$) positron diffusion to the surface and annihilation from the surface states. The reference spectrum from Si is shown in Fig. 1. Previous studies have demonstrated that the normalized curves contain distinct peaks and valleys at high momentum corresponding to annihilations with inner shell electrons[4].

The result obtained from Si containing divacancies is shown in Fig. 2. The normalized curve for defected sample has more counts in the central region and fewer counts at high Doppler shifts. When positrons are localized near an open-volume defect site, they are more likely to annihilate with the outer electrons of the neighboring atoms than a regular solid. So in a pure material, containing no foreign atoms, the positron localization at an open-volume defect will produce a reduction in annihilations involving high-momentum core electrons. However, if a vacancy-like defect has an element different from the host material

Figure 2. The Dopple-broadened annihilation spectrum of Si containing divaccancies normalized to bulk Si. The divaccancies are generated by implanting Si ions into a Float Zone Si wafer.

at high doping levels the carrier densities do not follow the dopant concentrations. TEM studies show no Sb precipitates and EXAFS studies show no signature for Sb-Sb bonding. The PAS studies on this system showed the formation of Sb-vacancy complexes at high doping concentrations. It is important to realize that Sb can be detected using this technique only if it is tied to an open-volume defect that will trap positrons. When Sb atoms are located at lattice sites and are activated, the ionized impurity atom will repel positrons.

Figure 3. The normalized DBAS for Sb doped LT-MBE Si. Results from pure Sb also is provided.

attached to it, the tail region of the normalized curve will show peaks and valleys that are characteristic of the atomic levels of the impurity.

Thin Si films produced by molecular beam epitaxy at low temperature (LT-MBE) were studied using this technique to understand the problems associated with the dopant (Sb) activation at high doping limits. The S-parameter measurements show that high quality Si films can be grown at low temperatures[6]. The low temperature MBE allows to produce films with dopant densities exceeding the solid solubility limit. However, the Hall measurements show that

Fig. 3 show results from LT-MBE Si films doped with Sb atoms at concentrations of 9.8×10^{19} , 5×10^{20} , 1.09×10^{21} , and $2.4 \times 10^{21} \text{ cm}^{-3}$. The first two values correspond to the linear regime where the dopants are fully activated. At the highest two values, the carrier concentrations were below the doping levels. Fig. 3 also shows the normalized DBAS curve for pure Sb. The data show a clear increase of the Sb signature at the highest two doping values commensurate with the saturation in activation.

The depth-resolved 2D-ACAR

Figure 4. 2D-ACAR spectra for SiO_2 -Si sample. (a) Spectrum with a beam energy of 2.0 keV at which 90% of positrons annihilate in the oxide. (b) Spectrum with a beam energy of 14.5 keV at which over 97% of positrons sample Si. (c) Spectrum from the interface region with a beam energy of 4.0 keV.

process to a thickness of $\sim 1170\text{\AA}$. Fig. 4 shows the 2D-ACAR results from bulk Si, SiO_2 -Si interface region, and SiO_2 . These results are obtained by changing the incident positron beam energy to implant the positrons in the respective regions. However, the spectrum collected from the interface region with a beam energy of 4 keV contains contributions from oxide and bulk Si. From the S-parameter versus energy measurements, the fraction of positrons annihilating in the bulk Si ($28\pm 5\%$) and oxide ($29\pm 5\%$) can be calculated. Therefore, the interface spectrum can be obtained by subtracting the weighted contributions of Si and oxide from Fig. 4(c). Fig. 5(a) shows the interface spectrum after removing the Si and oxide component.

To observe the fine structure of the interface spectrum, a broad component (defined as a Gaussian

Figure 5. (a) The interface spectrum obtained after the subtraction of the oxide and bulk spectrum. (b) Fine structure of the interface spectrum after the subtraction of a broad component from (a).

measurements were used to study the structure of the technologically important SiO_2 -Si interface[5].

The oxide layer was grown under a dry thermal

smoothed rotated average) arising from the core electrons and valence electrons which have a symmetric wavefunction is subtracted from Fig. 5(a). Fig. 5(b) shows the fine structure of the interface spectrum. The spectrum shows a sharp central peak along with a well-defined feature at the shoulders[5]. The central peak is indicative of positronium (Ps) formation. Ps is a bound state of the electron and positron, and the narrow central peak arises from the para-Ps decay. The Ps formation signals the presence of microvoids at the interface. From the observed FWHM of the central peak, the size of the microvoids is calculated as $11.9(9)\text{\AA}$ [5]. From the intensity of the Ps peak, it is also estimated that 6(1)% of positrons reaching the interface are trapped at the microvoids and form Ps. Recent theoretical simulations of the interface structure of Hybertsen is consistent with this picture of a high concentration microvoids at the interface[7]. The structure in the shoulder region of the interface spectrum is suspected to be caused by the positrons trapped at the Si dangling bonds (P_b centers). More systematic studies using metal-oxide-semiconductor structures with thinner oxides are underway to explore these structures in more detail.

4. Conclusion

We discussed some of the recent developments in depth-resolved positron annihilation spectroscopy of defects in semiconductors. These measurements provide a more detailed picture of the electron momentum distribution around the open-volume defect sites.

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References

1. *Positron Solid State Physics*, Proceedings of the International School of Physics "Enrico Fermi", Eds. W. Brandt and A. Dupasquier (North Holland, Amsterdam) (1983).
2. P.J. Schultz and K.G. Lynn, *Rev. Mod. Phys.*, **60**, 701 (1988).
3. Cs. Szeles, P. Asoka-Kumar, K.G. Lynn, H.-J. Gossmann, F.C. Unterwald, and T. Boone, *Appl. Phys. Lett.*, **66**, 2855 (1995).
4. P. Asoka-Kumar, M. Alatalo, V.J. Ghosh, A.C. Kruseman, B. Nielsen, and K.G. Lynn, *Phys. Rev. Lett.*, **77**, 2097 (1996).
5. J.P. Peng, K.G. Lynn, P. Asoka-Kumar, D.P. Becker, and D.R. Harshman, *Phys. Rev. Lett.*, **76**, 2157 (1996).
6. P. Asoka-Kumar, H.-J. Gossmann, F.C. Unterwald, L.C. Feldman, T.C. Leung, H.L. Au, V. Talyanski, B. Nielsen, and K.G. Lynn, *Phys. Rev. B* **48**, 5345 (1993).
7. M.S. Hybertsen, Private Communication (1996).