Elemental semiconductors Si and Ge have diamond crystal structures. The atomic structures have valence configurations like $s^2p^2$. The bonding process can be viewed as the promotion of an $s$-electron to a $p$-electron to form $sp^3$ hybrids. This explanation accounts for the nature of the bonding since $sp^3$ hybrids form tetrahedral bonding patterns which match the symmetry found in the diamond and zinc blende structures. Such hybridisation arguments can provide a framework within which the important metallicity trend of the tetrahedral elemental semiconductors can be explained. Carbon in the diamond structure has a rather large band gap and that this gap narrows from carbon to silicon to germanium to tin. For tin the gap vanishes identically and for lead valence and conduction bands overlap. We can view this process as the indication of the requirement of more energy to promote an electron from $s^2p^2$ configuration, to the bonding $sp^3$ configuration as we descend column IVA of the periodic table. While the nuclear charge increase is exactly balanced by an increase in core electron number, the larger number of core electrons is more effective in screening the nuclear charge. Thus, the valence levels in germanium are less tightly bound compared to Si and this is reflected in the more metallic character of the germanium band structure. Another significant feature which distinguishes the heavier elements from the lighter elements is the effect of core electrons on the valence electrons through the core orthogonalisation effects. The spin orbit splitting in the valence band increases with increasing core [5.1].

The nature of the charge density in elemental semiconductors was studied by Chelikowsky and Cohen [5.2]. The lowest band is $s$-like and other three valence bands have a clear covalent bond in between two atoms. Hence the anisotropies in
Fig. 5.1: Long-slit ACPAR data from Ge along different directions (Erskine and McGervey)
Fig. 5.2: Long-slit ACPAR data from Ge along different directions (Shulman et al)
charge density arise mainly due to the upper three valence bands.

As far as the charge and momentum density studies are concerned, there are lots of theoretical and experimental data on Si and Ge. Erskine and McGervey were the first to carry out ACPAR measurements in Si and Ge and later on the experiment on Ge was repeated by Shulman et al. The data are reproduced in Figs. 5.1 and 5.2 [5.3,5.4]. The data of Shulman et al are found to have some finer structures, nevertheless, there have been an overall similarity with the data of Erskine and McGervey. The ACPAR data as obtained by Erskine and McGervey along (100) and (110) directions show a flat region in the low momentum region, whereas along (111) direction it shows a sharp peak. In Shulman et al data there are dips in the low momentum regions in the corresponding directions instead of a flat region. But the shape of (111) direction remains same. The two-dimensional ACPAR data reveal more dip at the peak position than the long slit ACPAR data [5.4,5.5]. There are sharp cut offs in the (110) direction at 6.5 and 6. mrads of Si and Ge data respectively.

It is seen from Figs. 5.1 and 5.2 that they are not identical in the low momentum regions. As discussed in (2.45) the motion of positron at room temperature yields a resolution of 0.5 mrad. The point defects present in the samples contribute at the low momentum regions of the profiles. These two effects can smears the dips at the low momentum region of the profiles. Shulman et al performed their experiments at 77 K and with a magnetic field put around the positron source, they accumulated around one lakh counts at the peak of the profile. Further they annealed their samples and performed positron lifetime measurement before taking the ACPAR data. The intensity of the second component of the two-component fitting was found to be small ensuring the absence of major point defects in the
sample. For these reasons the dips are clearly seen in the profiles along (100) and (110) directions. But Erskine and McGervey performed their experiments at room temperature without properly annealing the samples. Therefore the dips are absent in their data. Hence a good statistics in the counts, good resolution of the set up, low temperature cryostat and well annealed samples are needed to observe the dips at the peak of (100) and (110) directions.

It is observed that in heavily doped semiconductors, the density of conduction band electrons in n-type or valence band holes in p-type semiconductors are changed in comparison to the density of valence electrons of intrinsic semiconductors [5.6]. The positrons are generally repelled by the holes and attracted by the electrons. Hence the annihilation properties in the heavily doped semiconductors are expected to change in comparison to the intrinsic semiconductors. But both the positron lifetime and ACPAR data showed no such evidence confirming that the density of holes in the valence bands and electrons in the conduction bands were too small to change the annihilation patterns [5.4].

In order to understand the detail nature of the profiles the simple theoretical methods were followed.

5.1. Theoretical Methods

(a) Jones Zone Model

This model was introduced by Erskine and McGervey which took a free electron picture. For diamond and zincblende structure, the structure factor is particularly large for the set of \{220\} planes. The volume bounded by these planes holds just four electrons per atom, so if the energy gap were large enough this volume could still contain all of the occupied states, thereby accounting for the semiconducting properties of Si and Ge. The regular dodecahedron formed by the set of \{220\}
Fig. 5.3: The Jone's Zone

Fig. 5.4: Area of cross sections through Jone's zone perpendicular to different crystallographic directions. A 1-mrad-square resolution function has been folded on each curve.
planes is known as Jones zone (Fig. 5.3). This behaves like a Fermi surface in semiconductors. Since the area of the Fermi sphere along a particular direction is considered as the CP and ACPAR data along that direction in free electron picture, it is worth taking the cross sectional areas of Jones zone along different directions to interpret the CP and ACPAR data. The three cross sectional areas are shown in Fig. 5.4. The area along (110) shows a surprising similarity with the experimental data whereas in other two directions the theoretical and experimental data deviate considerably. The cross sectional area along (100) direction is sharply peaked and along (111) is flat at the peak which is just opposite to that observed in experimental data. Thus, it is not easy to understand all the features as seen in the experimental data employing this model. So there arises the necessity of a more sophisticated model to explain the data.

(b) Nearly Free Electron Model

The periodicity of the lattice with extended zone scheme was taken in NFE model to account for the discrepancies in the free electron model. Assuming that the positron wave function is constant, the momentum distribution for nearly free electron model is

\[ |A(k)|^2 \frac{1}{4} \left[ 1 \pm x(1 + x^2)^{-\frac{3}{2}} \right] \]  

where

\[ x = \frac{G}{\frac{1}{2} G - k}/E_{gap} \]  

\[ E_{gap} \] is the band gap energy taken as 5 eV, \( G \) is a reciprocal lattice vector of the crystal, and \( k \) is the wave vector of the electron wavefunction. The upper and lower signs refer to the upper and lower bands. Using (5.1) one can calculate the CP or ACPAR data along different crystallographic directions.
Fig. 5.5: Anisotropy of the cross-section areas taken through the Jone's zone for diamond, Si and Ge. $J_{100} - J_{110}$ is on the left and $J_{100} - J_{111}$ is on the right. B. is the Jone's zone boundary.

Fig. 5.6: Anisotropies of the Compton profiles at equal electron density for diamond, Si and Ge. $J_{100} - J_{110}$ is on the left and $J_{100} - J_{111}$ is on the right.
The same opposite nature of the theoretical and experimental data was observed along (111) direction in the low momentum region. Reed and Eisenberger calculated the anisotropies like \( J(q)_{100} - J(q)_{110} \) and \( J(q)_{100} - J(q)_{111} \) from Erskine and McGervey Jones zone data which are plotted in Fig. 5.5 and the corresponding experimental anisotropies are also plotted in Fig. 5.6 [5.7]. It is found that the experimental and theoretical anisotropies for \( J(q)_{100} - J(q)_{110} \) have excellent agreement whereas for the other anisotropy \( J(q)_{100} - J(q)_{111} \) the agreement is good for diamond, but for Si and Ge the anisotropy has a poor agreement. This tempted Reed and Eisenberger to conclude that the anisotropy between (100) and (110) would depend on the shape of the Jones zone, but the anisotropy between (100) and (111) would depend on the detailed nature of orbitals taking part in bonding. Moreover, the three scaled CP data do not match with each other. Hence the theoretical calculations based on band structure method were needed to calculate CP and ACPAR data to explain these peculiar shapes.

(c) Band Structure Calculations

The first theoretical calculation was done to evaluate the CP and ACPAR data in Si by Stroud and Ehrenreich [5.8]. They calculated an anisotropic positron wavefunction by taking a realistic potential from the experimental charge density data. The matching between experimental and theoretical anisotropy between (100) and (111) directions in ACPAR data was excellent. Their theoretical calculation of the anisotropy of CP between the same directions also agreed well with the CP data of Reed and Eisenberger very well (Fig. 5.7). The effect of positron wavefunction was to increase the anisotropy at the low momentum region due to anisotropic positron wavefunction in the interstitial positions. The individual profiles did not match with the experimental data because the core orthogonalisation term was neglected
Fig. 5.7: Calculated anisotropy for the angular correlation distributions in Si (solid curve) compared with experiment (dashed curve).
in pseudopotential theory. But the theoretical anisotropy did not depend on the changes of the potentials. It could have been due to the fact that the anisotropy came from the k-dependence of the wavefunctions which was ultimately accounted for the Jones zone model as suggested by Reed and Eisenberger. But the subsequent calculation by Nara et al confirmed that all the anisotropies were independent of the potentials [5.9]. The reason of this is that the valence bands and the corresponding wavefunctions do not change with the changes of the form factors; but only the energy gap and the conduction bands change. The theoretical anisotropy between (100) and (111) directions had good agreement with the experimental anisotropy in Si, but in Ge it has a sign change at the origin. The scaling of the individual CPs did not match because the increase in core electrons affected the valence wavefunctions because of the core orthogonalisation term. Later on the more exact discrete variational LCAO method was employed by Seth and Ellis to calculate CP along different directions of Si which had a much better matching with the experimental data than the pseudopotential theory [5.10]. Unfortunately the theoretical data in other semiconductors by the same method are not calculated for a better comparison. This obviously confirmed that the nature of the wavefunctions ultimately decides the inapplicability of the Jones zone picture to explain the features in any direction.

5.2. The Effects of Bonding in Momentum and Position Space

Apart from the features which are either due to momentum space occupancy or due to anisotropy of the wave functions, there are some extra features in the data which very much depend on the detailed nature of bonding. In addition, one also sees Umklapp components. The long-slit ACER data are further affected by many body correlation effects and it is necessary to see how these effects affect the
Fig. 5.8: The nature of bonding along (100), (110) and (111) directions
CP and the ACPAR spectra as well as the derived \( B(r) \) function.

(a) The \( sp^3 \) Orbitals in Different Directions

The first ACPAR data in oriented graphite along c-axis showed a marked dip at the low momentum region, but in the direction perpendicular to c-axis the data had a sharp peak [5.11]. The same feature was observed by subsequent point slit measurement by Columbino et al who interpreted their data in a simple theoretical model [5.12]. They explained that the dip came from the presence of \( \sigma \) and \( \pi \) bonds along c-axis, whereas in the other axis the sharp peaking effect was due to the \( \sigma \) bond only. The CP data measured along the same directions did not show any such structure at the low momentum region which was also corroborated by recent theoretical calculations [5.13,5.14]. It is because of the fact that the sampling of the \( \sigma \) and \( \pi \) bonds by positrons is different from that of gamma rays. The behaviour at the low momentum region is expected to come from the same physical picture. The \( sp^3 \) hybridised orbitals have \( \sigma \) bond along (111) direction. As shown in Fig. 5.8 the interaction between second neighbour \( \sigma \) bonds is equivalent to introducing a \( \pi^* \) bond interaction between neighbouring atoms. The admixture of \( \sigma \) and \( \pi^* \) bonds make a dip at the peak of the profile along (110) and (100) direction [5.23].

(b) Umklapp Components

In high momentum region the ACPAR data along (110) direction in Ge showed a marked shoulder around \( \theta = 12 \) mrad. This was attributed to the so called Umklapp components. We have in (2.45) that the momentum density not only contributes at \( p = k \) but also at \( p = k + G \) with a relative strength given by the square of the Fourier coefficients \( |D_{\nu k}(G)|^2 \) of the positron-electron Bloch wave state. We note that for \( p_z \) along the (110) direction, the translations \( p = k + G \) of the electrons with \( k \) on the boundary of the first Jones and \( G = \{202\} \) (in units of \( \frac{2\pi}{a} \))
carry the face of the Jones zone parallel with itself (perpendicular to \( p_z \)), so that the centre of the Jones face is moved to the points \( \{312\}, \{312\}, \{132\} \) and \( \{132\} \). Thus the planar integration of the long slit geometry will reach these Umklapp images of the Jones' zone at the \( p_z = 2\sqrt{2}(\frac{2\pi}{a}) \) mrad position. The second Umklapp component is not visible in the data due to low counts in the data at higher momentum region. Similarly (100) direction has \( p = k + G \) at \( \{302\}, \{320\}, \{122\}, \) etc. and (111) direction has the values \( \{313\}, \{331\}, \{133\}, \) etc. The Umklapp images were not visible along (100) and (111) directions. Columbino observed the shoulders in point slit measurements along (111) direction [5.15]. He interpreted them to come from the \( sp^3 \) hybrids only. But the shoulders were absent in his experimental data along (100) and (110) directions. In CP data such structures were very hard to observe because there were oscillations in that region due to deconvolution technique. Unfortunately the Umklapp components were not yet obtained from the theoretical data. In fact, there is no rigorous theoretical ACPAR data in semiconductors. The OPW calculation in Al showed the Umklapp images which are absent in pseudopotential theory [5.16]. Hence an OPW computation to evaluate the ACPAR data in different crystallographic directions of various semiconductors are neeeded to justify the experimental results.

(c) Many Body Correlations

The explanation for the many body correlations in semiconductors was done in the Chapter 2. Fujiwara established this by comparing the experimental data along (110) direction with the theoretical data computed from IPM method in Si [5.17,5.18]. It was seen that at the zone face, the ACPAR data had a sharp slope whereas CP data fell slowly. In the high momentum region the ACPAR data remained less than the CP data. Comparing the measured ACPAR data along
Fig. 5.9: ACPAR data and CP data (SR) along (110) direction
(110) direction with the CP data along the same direction with resolution 0.084 a.u. shows the same behaviour [5.19] (Fig. 5.9). This sharp slope in (110) direction is the evidence of the enhancement and the other one is the dehancement effect. The same behaviour was obtained with Ge data [5.4]. Although the gap in Si is twice that of Ge, the changes in enhancements are expected to be small as observed by Dlubek in positron lifetime data [5.20]. The calculated core profile were subtracted from CP data whereas ACPAR data contained some core contributions. The ACPAR data without core would further reduce the high momentum region. Therefore, the dehancement effect which was argued primarily due to interband transitions was prominent in this comparison. But for a better picture, the evaluation of ACPAR data from a self consistent band structure calculation is highly required.

(d) The B(r) Functions

The autocorrelation function introduced in Chapter 2 has two features. It goes to zero values at the lattice constants and it has both negative and positive amplitudes. The zero crossings show the validity of Jones zone picture to describe the topology of the occupied states in semiconductors. However, the magnitudes of the oscillations decide the strength of bonding. For a covalent system, the oscillations are high because of the strong overlap of the orbitals and for ionic system it is much reduced. The amplitude of oscillations in $B(z)$ function along (110) direction in Si was large and $B(z)$ along (111) direction had less oscillations and (100) direction had a little oscillations only [5.21]. These are coming because the separations in atoms in different crystallographic directions are not same. As shown in Fig. 5.8 we find that the atomic separations are small in (110) direction. The atom siting at $\frac{\sqrt{3}}{4}$ along (111) direction yields more oscillations than (100) direction because the separation of the atoms is largest in that direction. Comparing the autocorrelation
Fig. 5.10: Autocorrelation function for Si and Ge along (110)
function along (110) direction in Si and Ge in Fig. 5.10, it is found that the dip in Si is more than in Ge. It is because of its larger lattice constant. Hence the autocorrelation function is more diffused in Ge than in Si. Sakai et al in their CP measurement with SR source had found a zero shift in their autocorrelation function along (110) direction. But the results might not be accurate because the statistical errors were their in their data analysis [5.19].

The $B^{2\gamma}(z)$ functions for angular correlation data in all directions are not available in literature. The $B^{2\gamma}(z)$ function along (110) direction was obtained by Berko et al which is plotted in Fig. 5.11 [5.22]. It is found that the oscillations in ACPAR data are much more than that of CP data and spread to the high position. It is mainly due to the better resolution of the experiment. There is pronounced zero shift in the first and second lattice vectors; but the separation of the zeroes is same as observed in Compton data within the statistical accuracy. The reason for this zero shift is mainly due to the presence of the anisotropic positron wavefunctions.

Pattison et al measured the anisotropy between (111) and (100) in silicon and diamond [5.23]. Due to the large separation of the lattice points, the (100) direction can be thought of as a nonbonding direction. So the anisotropy gives the informations about the bonding in (111) direction. They found a pronounced negative dip at the first bond length. In order to understand this feature they took the simple model of Weyreich et al to calculate the $B(r)$ function [5.24]. The $B(r)$ for a molecular orbital (MO) can be expressed in terms of the atomic orbitals (AO) $\phi_A(r)$ and $\phi_B(r)$ as,

$$B(r) = [2(1 \pm S)]^{-1} \times$$

$$\left[ B_A(r) + B_B(r) \pm \int \phi_A(s + r + R_b)\phi_B(s)ds \pm \int \phi_B(s + r - R_b)\phi_A(s)ds \right]$$

(5.3)

where $B_A(r)$ and $B_B(r)$ are the autocorrelation functions resulting from the atomic
Fig. 5.11: $B_{110}^{2\gamma_0}(r)$ of Ge. (o) corresponds to the lattice positions.

Fig. 5.12: Autocorrelation anisotropy between (111) and (100) direction of diamond; ( ), experimental data and (-), theoretical data.
orbitals A and B respectively and S is the overlap integral between $\phi_A$ and $\phi_B$. If $\phi_A = \phi_B$ then,

$$B(r) = (1 \pm S)^{-1} \left[ B_A(r) \pm \frac{1}{2} [B_A(r + R_b) + B_A(r - R_b)] \right] \quad (5.4)$$

At the bond distance (5.4) becomes,

$$B(R_b) = (1 \pm S)^{-1} \left[ B_A(R_b) \pm \frac{1}{2} [B_A(2R_b) + B_A(0)] \right] \quad (5.5)$$

This function shows an extremum arising from $\frac{1}{2}E_A(0)$ term. For a bonding ($p,p)\sigma$ MO the $p$ AOs are oriented antiparallel to each other (i.e. $\phi_A = -\phi_B$) and we can expect a negative extremum at the first bond length. Similarly for (110) direction ($p,p)\pi^*$ MO could produce a peak in $B(r)$ which lies at the second bond position as shown in Fig. 5.12.

A small negative peak is also present at the vicinity of the nucleus. This is present in both Si and Ge data. It is not clear why such a peak is there. Pattison et al interpreted this to arise from the systematic errors in the data analysis.

5.3. The Reconstruction of $\rho(p)$ in Si

Hansen et al used Fourier-Bessel method to reconstruct $\rho(p)$ from a set of exprimental and theoretical CP data in Si [5.23, 5.25]. They reconstructed $B(r)$ and $\rho(p)$ anisotropies in Si by taking 10 crystallographic directions (Fig. 5.13, 5.14) with four cubic harmonics expansions. Pattison et al took only six directions to reconstruct the anisotropies. The results were not very much different from each other. The experimental CP data shows a striking minima at the first bond length. As shown in Fig. 5.8, it is due to ($2p,2p)\sigma$ bond at the first bond length. In the $\rho(p)$ anisotropy data a positive peak is observed at that position. At the second bond length a striking maxima is observed which is due to the ($2p,2p)\pi^*$ bond.
Fig. 5.13: The $B(r)$ anisotropies in Si; contour intervals are 0.01 e. Full contours correspond to positive value, broken contours to negative value.

Fig. 5.14: The $\rho(p)$ anisotropies in Si; contour intervals are 0.01 e/au$^3$. Full contours correspond to positive value, broken contours to negative value.
Fig. 5.15: $\rho(p)$ of Si along (110) direction
In the $\rho(p)$ it is obtained as a positive peak. The reconstructed $\rho_{110}(p)$ from the theoretical data of Seth and Ellis is plotted in Fig. 5.15. It shows a behaviour expected from the completely filled band.
References


96


