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PHOTOEMISSION STUDIES OF 2p CORE LEVELS OF PURE AND HEAVILY DOPED SILICON

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Photoemission studies of 2p core levels of pure and heavily doped silicon[+]

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Abstract

The energy distribution curves of the 2p core levels of pure and heavily doped Si have been investigated using highly monochromatized (0.1 eV) synchrotron radiation (105 eV - 140 eV). Shifts and broadenings of the spectra with doping and with the energy of the exciting photons have been observed and interpreted in terms of the electrostatic band bending at the semiconductor surface and, for pure Si, of surface core shifts. The "absorption" spectrum of the 2p→conduction band transitions has been studied for the same materials with the partial yield technique. By combining the absorption spectra and the core level EDC's a value of $E_B = 0.18 \pm 0.2$ eV for the

core exciton binding energy is determined. Small differences in the 2p→conduction edge both with doping and with the energy of the exciting photons are observed and discussed.

Introduction

Optical transitions from core levels of solids, in particular semiconductors, to their conduction bands have been extensively investigated since the advent of synchrotron radiation.[1,2] They yield information about the structure and density of states of the conduction bands and, when combined with photoelectron spectroscopy measurements, about possible excitonic shrinkage of the excitation gap.[3] These transitions can be investigated by means of optical reflectance and transmittance measurements[4] and also electron energy losses.[5] The transmittance and energy loss measurements require the preparations of thin samples which is often difficult in highly crystalline form (i.e., for silicon, the object of the present investigation). This difficulty can be avoided by using the yield spectroscopy technique[6], i.e., the measurement of the photoelectric yield over a wide electron energy range. This yield is, because of the small average escape depth of the electrons, roughly proportional to the absorption coefficient.

The photoelectron spectroscopy measurements, based on the determination of the energy distribution curves (EDC) of photoelectrons emitted by monochromatic radiation, yield the position of the core levels with respect to the Fermi energy. Thus, in order to compare this work

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[+] physica status solidi to be published

[++] Work at the Max-Planck-Institut für Festkörperforschung supported in part by the Alexander von Humboldt Foundation with the optical absorption discussed above the position of the Fermi level with respect to the conduction band edge must be known. The determination of this position poses some rather basic difficulties if, as in the case of silicon and a number of other semiconductors, a large density of surface states is present which pins the Fermi energy at the surface and makes it nearly independent of that at the bulk.[7,8] The escape depth of photoelectrons is small (4 to 40 Å) and hence the core levels are usually obtained with respect to the surface Fermi level pinned by surface states. If the semiconductor is heavily doped, however, strong electrostatic band bending occurs near the surface in order to make the transition from the pinned Fermi level to the Fermi level of the bulk (the Fermi level remains flat; the bands bend). The core levels should follow the electrostatic potential which produces the band bending. Under these conditions the binding energy of the photoelectrons will depend on the exciting photon energy: If this energy is only a few eV above threshold the escape depth of the photoelectrons is relatively large ($\approx$ 40 Å [8,9]) compared with the barrier depth and the binding energy will approach that of the bulk. At higher photon energies the escape depth can be as small as 5 Å and the binding energy of the core levels, as determined in the EDS's becomes that at the surface (see Fig. 1).

Several inconclusive attempts have been made to observe changes in the binding energies of semiconductors with doping.[10] More recently[11] a change of the order of the gap (1.1 eV) was observed between n- and p-type silicon with $\approx 3\text{x}10^{19}$ carriers/cm^3

with Al K_α excitation (1486. eV), although the samples were coarsely ground in air and the vacuum rather poor (10^{-6} torr). More recently, Wagner and Spicer have observed shifts in the valence bands EDC's of silicon (cleaved in UHV) with heavy n- and p-doping for $\hbar\omega$ = 11.8 eV.[12] In this paper we present measurements of the photoelectron spectrum of the 2p core levels (EDC) of a series of Si samples including a nearly intrinsic and several heavily doped n and p-type ones cleaved in situ under ultrahigh vacuum. The measurements were performed with monochromatized synchrotron radiation, in order to be able to vary, by changing the exciting photon energy, the escape depth of the photoelectrons. The exciting photon energies $\hbar\omega$ were chosen between 115 eV (escape depth $\lambda \sim 25$ Å) and 135 eV ($\lambda \sim 4$ Å). For $\hbar\omega$ = 115 eV the escape depth is of the order of the penetration depth δ of the surface barrier in the heavily doped samples and therefore the binding energy of the bulk should, at least in part, be sampled. For $\hbar\omega$ = 135 eV λ is expected to be $\sim$4 Å.[9] Hence the measurements should reflect mostly the binding energy of the core levels near the surface. The observed variation of the average binding energy with $\hbar\omega$ (i.e., with escape depth) can be interpreted in terms of the model of a nearly filled and a nearly empty surface states band which has become will established[13] for the reconstructed (111) surfaces of Si[14].

In agreement with these ideas, the EDC's of the heavily doped samples show a broadening with decreasing $\hbar\omega$ which corresponds to the sampling of a wider range of binding energies. For the intrinsic samples, however, the broadening is observed with increasing $\hbar\omega$, thus suggesting it is due to a range of binding energies in the first few surface layers. This phenomenon is attributed to the electronic redistribution associated with the surface states, thus giving rise to a range of core level binding energies.

As already mentioned, by combining EDC's determination of binding energies of core levels with measurements of the corresponding absorption edge an exciton binding energy is usually obtained. The value 0.6 + 0.2 eV can be inferred for 2p levels of Si from the data of Ref. 14. Electron energy loss measurements indicate an exciton binding energy of about 0.9 eV[16]. We have performed measurements of the 2p absorption edge in our intrinsic and heavily doped samples, in order to determine the exciton binding energy and to investigate possible changes of the edge with doping.[16] When combined with the EDC's of the same surfaces, our measurements, performed by the partial yield technique, give 0.18±0.2eV for the excitonic binding energy. The shape of the absorption edge is found to be nearly the same for the intrinsic as for the heavily doped n-type samples, in agreement with Ref. 17. For the most heavily doped p-type samples, however, a slight sharpening of the edge is observed. This sharpening is tentatively explained as due to an exclusion of conduction band final states from the surface depletion layer in a way analogous to the surface quantization in depletion and inversion layers.[18]

Experimental details

The measurements were performed with synchrotron radiation from the DORIS storage ring, which was monochromatized by the FLIPPER-monochromator[19]. The photon resolution was 70 meV at ħω = 100 eV and 220 meV at ħω = 140 eV. The photoelectrons

were analysed and detected with a commercial double pass cylindrical mirror analyzer operating at a fixed energy resolution. Most of the yield spectra were measured with a bandpass of 4 eV whereas in the EDC work the resolution of the analyzer was set at 180 meV. The geometry of the analyzer is such that it accepts electrons in a conical shell with all possible polar angles between 0° and 90°.

The samples were cleaved in situ in UHV at a typical pressure of 2×10^{-10} torr. Since steps in the cleavage plane or oxidation may influence the surface states, the samples were checked against these problems by taking EDC's of the valence bands before and after each series of measurements.

Results

The EDC's obtained at several photon energies for the "intrinsic" ($n = 10^{14}$ cm^{-3}) and the most heavily doped n and p-type samples measured ($n = 8 \times 10^{19}$ cm^{-3} and $p = 1.6 \times 10^{20}$ cm^{-3}) are shown in Fig. 2. The intrinsic sample exhibits a well resolved $L_{III} - L_{II}$ doublet, especially at the lower photon energies (longer escape depth). For the n-type sample this spin-orbit doublet is not resolved for small ħω (106.8 eV) while it appears resolved at 113.7 eV seemingly broadening again at 130.6 eV. The p-type sample also shows some broadening for ħω = 121.6 eV with respect to the smaller exciting photon energies. The binding energies of Fig.2 are with respect to vacuum. With respect to te Fermi energy we found for the binding energy of the intrinsic sample($2p_{3/2}$) 99.2±0.1 eV and for the corresponding spin-orbit splitting 0.62±0.03 eV.

The positions of the L_{III} peaks observed for the various samples measured are displayed in Fig. 3 as a function of photon energy. On the lower abscissa of this figure the photon energy has been converted to escape depths using the value of 25 Å measured 5.5 eV above threshold by Allen and Gobeli[8] and the universal curve given by Spicer[9]. The differences in binding energies between n- and p-type samples increase with increasing escape depth, as expected from Fig. 1 and reach at 25 Å 0.8 eV, slightly less than the energy gap (1.1 eV).

Figure 4 shows the absorption edge for transitions from the 2p core levels to the conduction band obtained by measuring the partial yield of photoelectrons with energies between 0 and 4 eV on the 3 samples of Fig. 2. The data, which are very similar to the results reported earlier by other authors[3,15], display the two absorption edges L_{III} and L_{II}. The insert (x5) shows clearly how the $b_{III} - b_{II}$ doublet broadens with doping especially for the sample with $n = 8 \times 10^{19}\,cm^{-3}$. The onset of the edge, however, is nearly identical for the intrinsic and the heavily doped n-type sample and somewhat sharper for the p-type one.

Discussion

The data of Fig. 3 require for their interpretation the assumption of surface states. The density of surface states calculated by Schlüter et al.[13] can be approximated by a band of filled states and a band of empty states both with a width of 0.2 eV; for the purpose of the present calculation both bands can be assumed to be rectangular (see Fig. 12 of Ref.[13]). In order to fit our data best we found it necessary to increase the gap between filled and empty states from 0.17 eV, as given in Ref. 13, to 0.27 eV. This agrees with the gap observed in infrared absorption[20], a fact which, however, is also compatible with a lowest indirect gap of 0.17 eV if only direct transitions

are assumed to contribute to the infrared absorption between filled and empty surface states. Our model density of surface states is represented by the shaded rectangles in Fig. 3.

The sample parameters used in our calculations are listed in Table I. The Fermi levels of the p-type samples at room temperature were read off from the numerical calculations of Ref. 21. These of the n-type samples were calculated from Eq. (1) of Ref. 17.

The Fermi levels at the surface E_{FS} were calculated by solving the equation:

$$\int_{-\infty}^{+\infty} N_s(E)\ f\ (E-E_{FS})\ dE = n_s - n_v\delta \qquad (1)$$

where n_s is the number of atoms per cm^2 in a (111) plane ($n_s = 8 \cdot 10^{14}$), n_v the volume concentration of dopant atoms (taken positive for acceptors, negative for donors) $f(E-E_{FS})$ the Fermi function and δ the penetration depth of the space charge layer given by

$$\delta = \left(\frac{V_o}{2\pi e N}\right)^{\frac{1}{2}} \qquad (2)$$

where $\varepsilon = 12$ is the dielectric constant of Si and V_o the barrier height equal to $E_{FS} - E_{FB}$. n' takes into account the possibility of a charge transfer between the surface states and the bulk in the intrinsic case. Equations (1) and (2) must be solved self consistently in order to determine δ and V_o. Self consistency, however, is easy to achieve.

In order to obtain the average binding energy observed with monochromatic photons we must average the position dependent binding energy $E_B(z)$ over the depth of the space charge layer δ :

$$E_B(z) = E_{BV} + \frac{2\pi}{\varepsilon} eN(z-\delta)^2 \qquad (3)$$

Assuming a Schottky type space charge layer and integrating Eq. (3) we obtain:

$$E_B = E_{BV} + V_o \left\{1+2\frac{\lambda}{\delta^2}(\lambda-\delta) - 2e^{-\delta/\lambda}(\lambda^2/\delta^2)\right\} \qquad (4)$$

where E_{BV} is the binding energy of the core levels well inside the material. Using the parameters of Table I we obtain with Eq. (4) the solid lines of Fig. 3. It must be mentioned, however, that Eq. (4) assumes that only those electrons escaping normally to the surface are collected. In our experimental set up we have collected with the cylindrical mirror analyzer electrons emitted at angles with respect to the normal ranging from 0 to $\sim\pi/2$ In order to correct for this fact we introduce into Eq. (4) instead of λ the sampling depth:

$$\lambda' = \lambda\langle\cos\theta\rangle = \frac{2\lambda}{\pi} \qquad (5)$$

where λ is determined by the photon electron energy according to the universal curve.[9] In this manner we obtain the dashed curves of Fig. 3. With the exception of the most heavily doped p-type sample these curves represent rather well the experimental data, the difference between dashed and solid curve not being of much significance.

The calculations for the sample with $p = 1.6 \times 10^{20}\text{cm}^{-3}$ fit the data at low photon energies (large λ) but deviate considerably for small λ . A similar anomaly was observed by Allen and Gobeli (see Figs. 3 and 4 of Ref. 8):

The work function for $p > 10^{20}\text{cm}^{-3}$ was seen to decrease with increasing doping contrary to the predictions based on density of surface states models similar to that of Fig. 3. A possible explanation of this anomaly may lie in a strong dependence of the density of surface states, in particular the surface gap on doping. This could be the result of a decrease in the amount of surface reconstruction with doping which may result in a closing of the gap between filled and empty surface states. We should point out that the dashed lines of Fig. 3 suggest that a similar effect may be occurring also for the heavily doped n-type samples (see also Fig. 4 of Ref. 8). The broadening of the L_{II-III} doublet in Fig. 2 for $p = 1.6 - 10^{20}\text{cm}^{-3}$ and $\hbar\omega = 121.6$eV could be related to fluctuations along the surface of the amount of surface reconstruction, associated with doping fluctuations.

Fig. 5 shows a fit of the doublets of Fig. 2 (a) for $\hbar\omega = 105.6$ and 130.1 eV with two Lorentzians, one for each spin-orbit split component. The corresponding widths ΔE (FWHM) so obtained are displayed in Fig. 6a as a function of electron energy above threshold. The experimental curves of Fig. 5 contain also the line width of the exciting radiation and the resolution of the electron analyzer, both shown also in Fig. 6a. The resolution functions of monochromator and analyzer can be assumed to be

Gaussian, as proven by measuring the core lines of gaseous argon. We, therefore, also fitted the experimental data of Fig. 5 with a lorentzian convoluted with a gaussian of the appropriate width. The fit so obtained was, within the accuracy of the drawing, the same as that of Fig. 5. In this manner the corrected line widths (FWHM) of the two doublet components shown in Fig. 6 b were obtained. The width of the $2p_{1/2}$ component seems ≈ 0.1 eV larger than that of the $2p_{3/2}$ one, a fact which cannot be attributed to additional Coster-Kronig decay of the $2p_{1/2}$ line (the $2p_{3/2}$-$2p_{1/2}$ splitting is much smaller than the ionization threshold). We cannot offer any microscopic explanation for this difference which may, thus, be an artifact of the fitting procedure.

The result of Fig. 6 b indicate a doubling of the line width as the surface is approached. The reconstructed (111) surface is supposed to be polar with some atoms positively charged and other negatively. Hence fluctuations in the chemical shifts of the atoms must occur for the first few surface layers. These fluctuations could easily account for the observed broadening. We proceed now to estimate the fluctuations in the first surface layer in a manner similar to the calculation of chemical shifts of ionic materials given in Ref. 22. We write for the negatively charged surface atoms:

$$\Delta E = \left(\frac{1}{r} - \frac{\alpha}{R}\right) \Delta q \qquad (6)$$

where α is the Madelung constant of the surface (assuming it is formed by rows of neighbouring atoms with opposite charges) R the distance between surface nearest neighbours, r an average distance between the negative surface ion and the excess negative

charge produced by the reconstruction, and we have evaluated the Madelung constant of the surface to be $\alpha = 1.4$. The evaluation of r is more difficult since it requires a volume integration of the excess charge. From Fig. 13 of Ref. 13 we obtain $r \approx \frac{1}{2} R \approx 1.17$ Å and hence for a charge of one electron transferred by reconstruction we find $\Delta E \sim 3.7$ eV.

Hence for the first surface layer chemical shifts of the order of ≈4 eV are expected and, in view of the resolution of Fig. 2, there is the possibility of observing the resolved levels of the first layer of atoms, especially if angular resolved measurements with large angles were performed. According to Fig. 13 of Ref. 13 the surface states charge extends weakly to the second, third and fourth layer. The charge density between these layers is approximately one fourth of that around the first layer: Hence chemical shifts ≈ 1/4 x 4 eV ≈1 eV are expected for these layers. These shifts can account for the increase in width with decreasing escape depth displayed in Fig. 5.

The same behaviour can be observed taking partial yield spectra with different final state energies. The corresponding spectra are shown in Fig. 7. In these measurements, the energy window of the analyzer had a width of about 4 eV and the center was set at E_F = 1 eV and E_F = 20 eV, respectively. Since electrons with a kinetic energy of 20 eV have a shorter escape depth than those with a kinetic energy around 1 eV, the spectrum for E_F = 20 eV is more surface sensitive. Correspondingly the absorption edge at the surface is broader than in the bulk, which is in agreement with the increase of the photoemission linewidth. The width of the L_{III} absorption edge changes from 280 meV to 490 meV by going from 1 eV to 20 eV kinetic energy of the electrons, whereas the linewidth of the directly measured photoelectrons coming out of the 2 p3/2 levels changes, from 220 meV to 450 meV (after correction for photon width and analyzer resolution). Two consistent and independent observations of an increase in core level line width near the surface have thus been obtained. We should also remark that according to Fig. 3 a shift of $E_B \simeq 0.1$ eV of the core level binding energy also takes place for the intrinsic sample as the surface is approached.

We now try to analyse the "blue" shift observed for the low enery tail of the absorption edge of the $p = 1.6 \times 10^{20} cm^{-3}$ sample of Fig. 4, in particular whether it can be attributed to quantization of the final conduction states in the surface depletion layer. From Eq.(10 b) of Ref. 18 we calculate for this sample an energy for the first bound conduction state of 0.4 eV above the bottom of the conduction band. This is more than the height of the barrier itself and hence the first conduction states near the surface are expected to lie at about the same height as the bulk ones. A "blue" shift of the order of 0.3 eV can thus be expected. While this interpretation appears to be in agreement with the spectra in Fig. 4 we should mention that the blue shift showed up only with low kinetic energies E_K for which the spectra contain partly a large volume contribution. The fact that this shift was not as pronounced in surface sensitive spectra (high E_K) can be attributed to the broadening of the core levels as shown in Figs. 6 b and 7.

In order to determine the excitonic binding energy associated with the absorption spectrum of Fig. 4 we deposited gold on the samples of Fig. 2 so as to find the binding energies E_B with respect to the Fermi energy of gold (≃ Fermi energy of our sample). We then take the Fermi energy with respect to the top of the valence band $(E_F - E_V)$ for each sample from Fig. 2. Using the known value of the indirect gap at room temperature $E_i = 1.1$ eV, we find for the binding energy of the $2p_{3/2}$ levels with respect to the bottom of the conduction band:

$$E_C - E(2p_{3/2}) = E_B - (E_F - E_V) - E_i = 99.94 \pm 0.15 \text{ eV}.$$

We judge the point labelled L_{III} in Fig. 3 (at 99.76 ± 0.05 eV) to be the most reasonable assignment of the edge in view of that the width ofthe corresponding stretch of the absorption edge approximately equals the monochromator resolution. We thus find for the excitonic binding energy 99.94 - 99.76 = 0.18 ± 0.2 eV, basically negligible and much smaller than previously reported.[15,16] One could increase our value of the binding energy if one takes for the position of the excitonic edge the onset of the absorption tail at 99.0 eV in Fig. 3. However, such assignment would not be reasonable since this tail can be accounted for in terms of core level width (~0.2eV) and monochromator resolution (~0.1 eV). We should point out that the fact that the binding energy of the core excitons is negligible within the experimental error does not mean that excitonic effects are absent in the $2p^{3/2}$ edge. The steepness of this edge, as compared with that of the density of conduction states can still be taken as evidence for excitonic effect at the edge.[3]

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n_v (cm^{-3})	$p=1,6\times10^{20}$	$p=2,5\times10^{19}$	$p=6,8\times10^{18}$	$n=10^{14}$	$n=8\times10^{19}$
E_{FB}	-105	-6	+37	E_i -310	E_i +60
E_{FS}*		260	300	340	430
$E_{FS_{theor.}}$+	233	259	277	330	428
V_o+	338	265	240	460	732
δ(Å)+	16,7	37,8	68,4	$2,47\times10^4$	34,8
$\frac{n_v\delta}{N_o}$(%)	-3,2	-1,2	-0,6	$+3\times10^{-3}$	+3,5
$E_{FS_{theor.\ corr.}}$**	232	255	270	300	427
V_o**	337	261	233	490	733
δ(Å)**	16,7	37,2	67,4	$2,55\times10^4$	34,8

Table I. Values of the parameters required for the calculation of the solid curves of Fig. 3. All energies are in meV. E_i is the indirect gap energy(1.1 eV).

* Measured, from Ref. 8

+ Calculated assuming $n' = 0$ in Eq. (1)

** Calculated for $n' = 0.002\ n_s$ so as to obtain agreement between $E_{FS_{theor.}}$ and that observed in Fig. 3 for the sample with $n = 10^{14}$.

Figure Captions

1. Schematic diagram of the core level shifts associated with space charge layers in heavily doped silicon.

2. Experimental observation of the shifts in the 2p (L_{III} - L_{II}) core lines of silicon with doping the kinetic energies are referred to the vacuum level.

3. Shifts in the position of the L_{III} line of Fig. 2 as a function of doping and photon energy. The solid and dashed lines were calculated as described in the text. The band and surface states (shaded) diagram assumed for the calculations is given on the left vertical axis.

4. Yield spectrum (= absorption) spectrum of pure and heavily doped silicon for the L_{III} - L_{II} absorption edge.

5. L_{III} - L_{II} core lines of pure silicon (solid line) and corresponding fits with two lorentzian functions of widths given in Fig. 6a.

6. (a) Widths required for the lorentzian fits of Fig. 5 and corresponding analyzer (CMA) and monochromator (Flipper) resolutions.

   (b) Width required for the lorentzian fits of Fig. 5 after gaussian deconvolution of the monochromator and analyzer resolutions.

7. Yield spectrum of pure silicon for two different positions of the center of the 4 eV analyzer window.

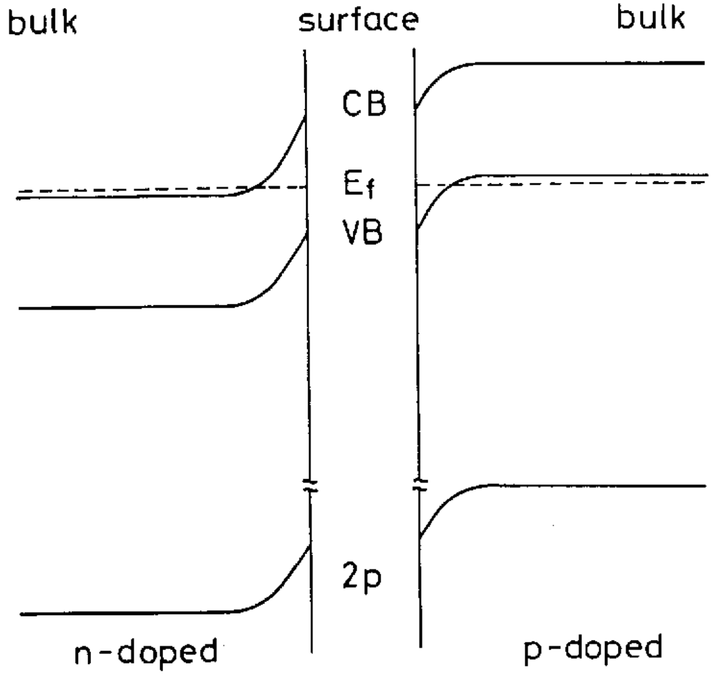
bulk
surface
bulk
CB
E_f
VB
2p
n-doped
p-doped

Fig. 1

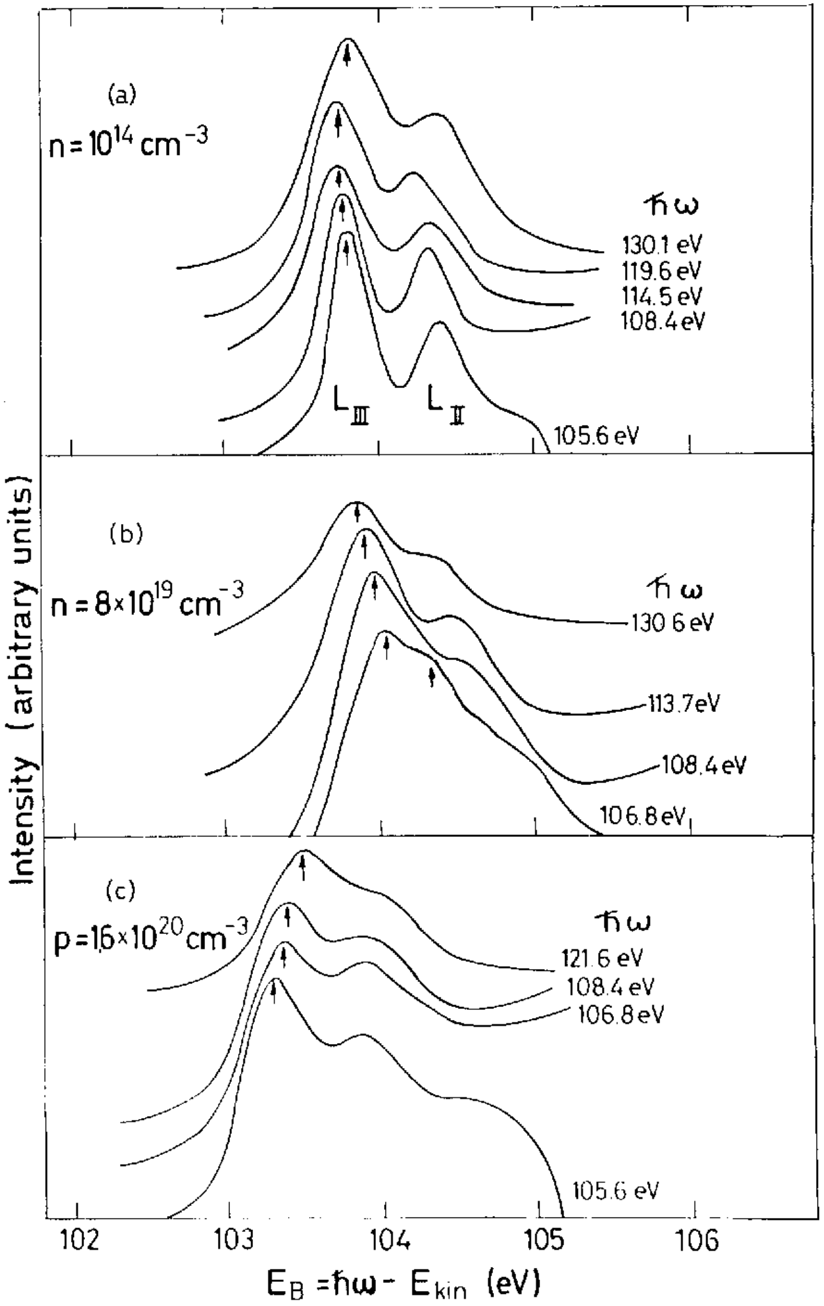
(a)
$n = 10^{14}\,cm^{-3}$
ħω
130.1 eV
119.6 eV
114.5 eV
108.4 eV
105.6 eV
L_{III}
L_{II}
(b)
$n = 8 \times 10^{19}\,cm^{-3}$
ħω
130.6 eV
113.7 eV
108.4 eV
106.8 eV
(c)
$p = 1.6 \times 10^{20}\,cm^{-3}$
ħω
121.6 eV
108.4 eV
106.8 eV
105.6 eV
Intensity (arbitrary units)
102
103
104
105
106
$E_B = \hbar\omega - E_{kin}$ (eV)

Fig. 2

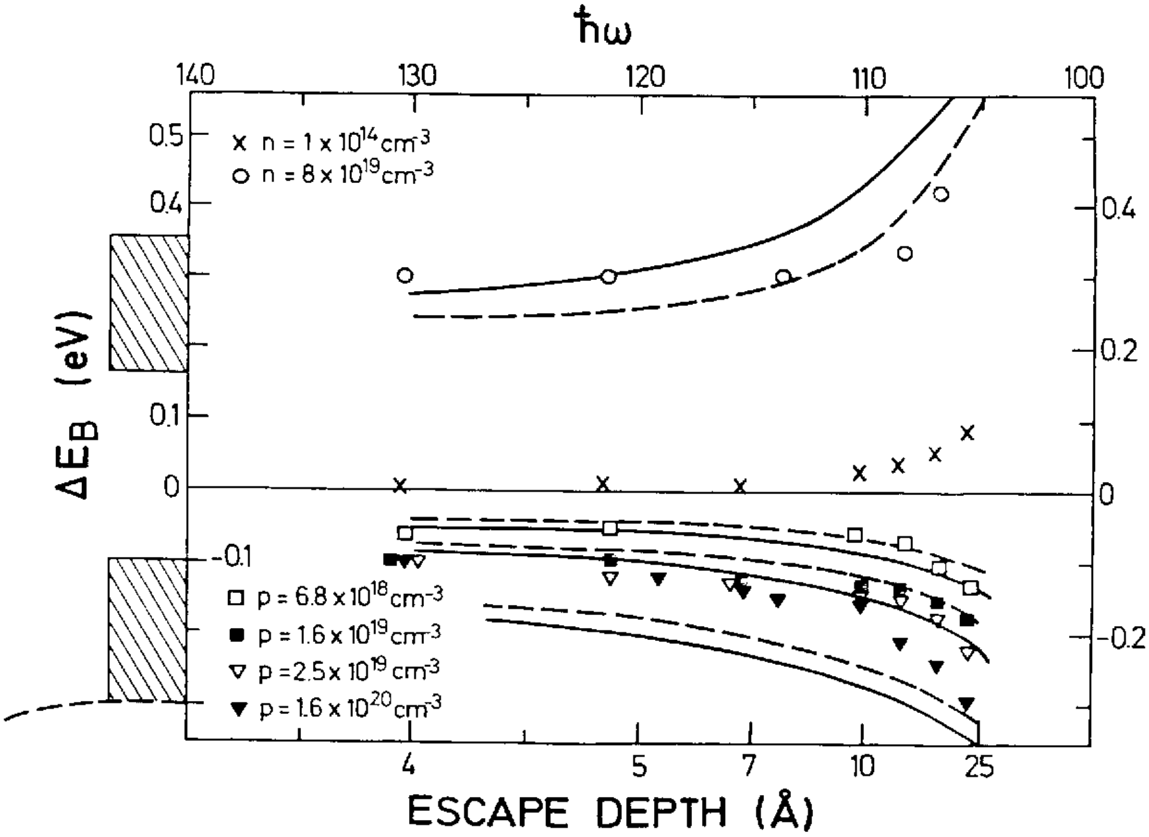
ħω
140
130
120
110
100
0.5
0.4
0.1
0
-0.1
0.4
0.2
0
-0.2
ΔE_B (eV)
x n = 1 x 10^14 cm^-3
o n = 8 x 10^19 cm^-3
□ p = 6.8 x 10^18 cm^-3
■ p = 1.6 x 10^19 cm^-3
▽ p = 2.5 x 10^19 cm^-3
▼ p = 1.6 x 10^20 cm^-3
4
5
7
10
25
ESCAPE DEPTH (Å)

Fig. 3

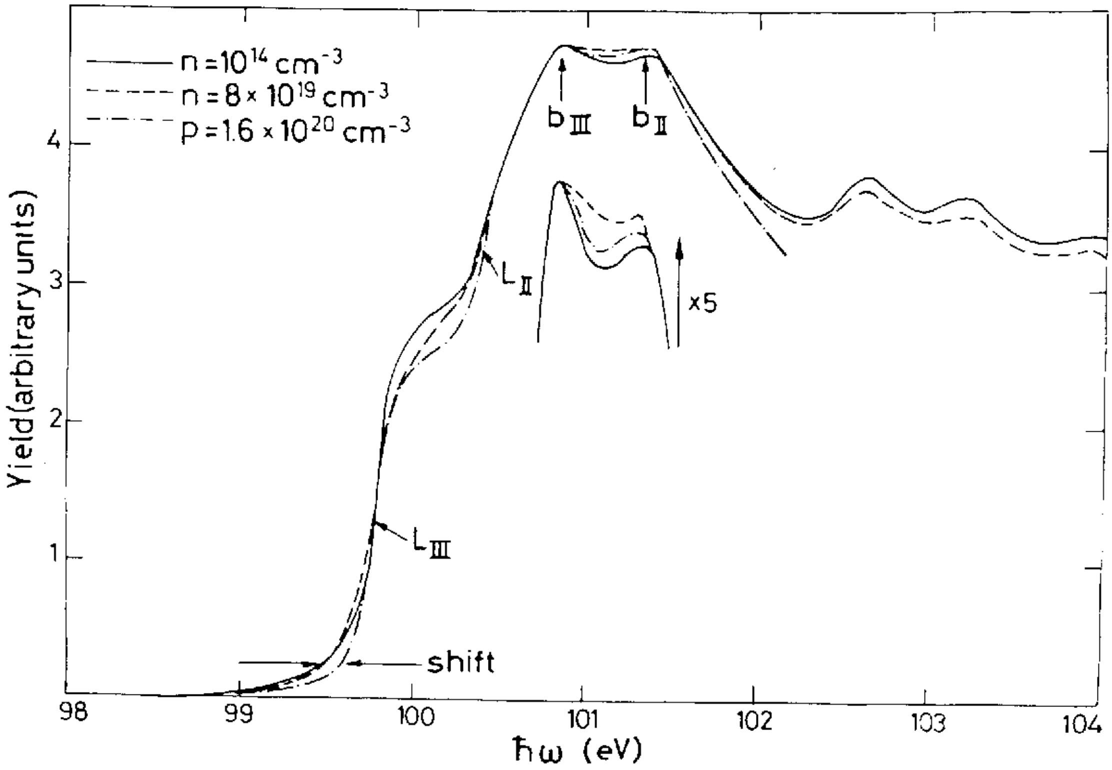
n = 10^14 cm^-3
n = 8 x 10^19 cm^-3
p = 1.6 x 10^20 cm^-3
b_III
b_II
L_II
L_III
x5
shift
Yield (arbitrary units)
1
2
3
4
98
99
100
101
102
103
104
ħω (eV)

Fig. 4

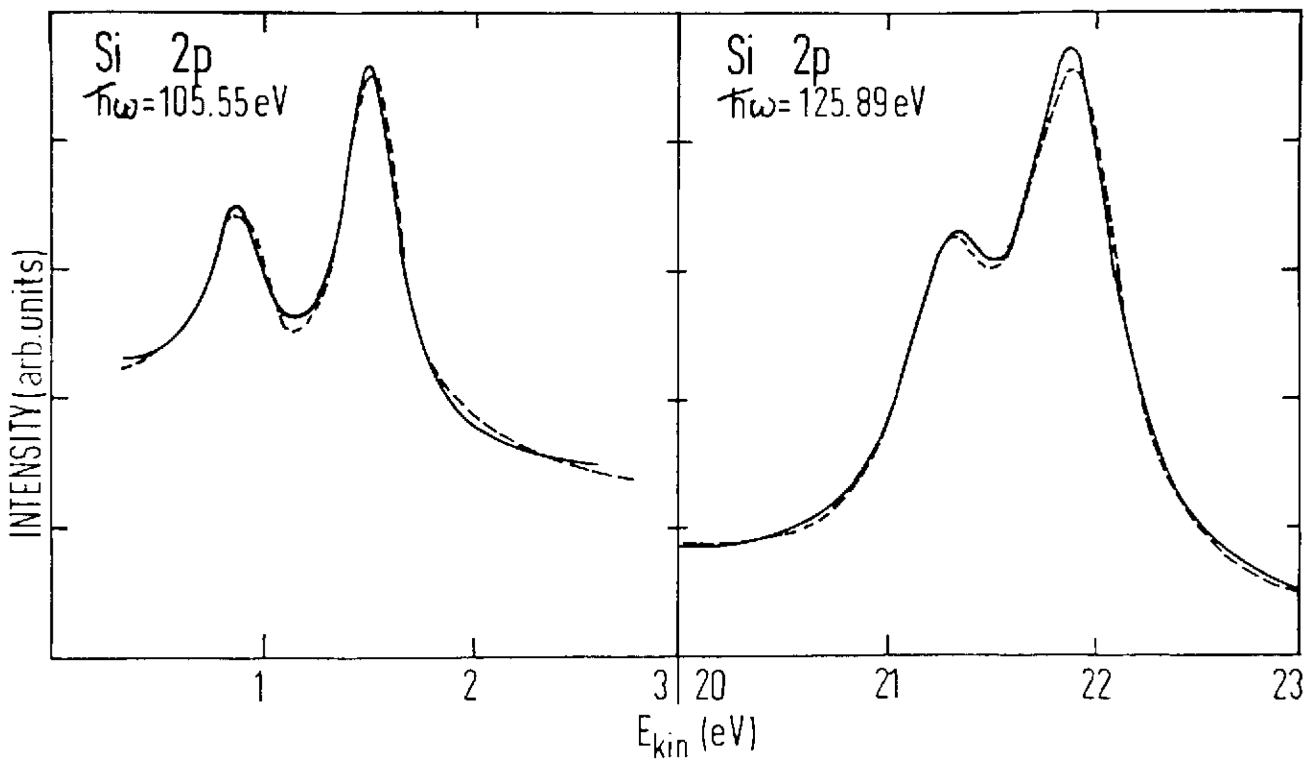
Si 2p
$\hbar\omega$=105.55eV
Si 2p
$\hbar\omega$= 125.89eV
INTENSITY(arb.units)
1
2
3
20
21
22
23
E_{kin} (eV)

Fig. 5

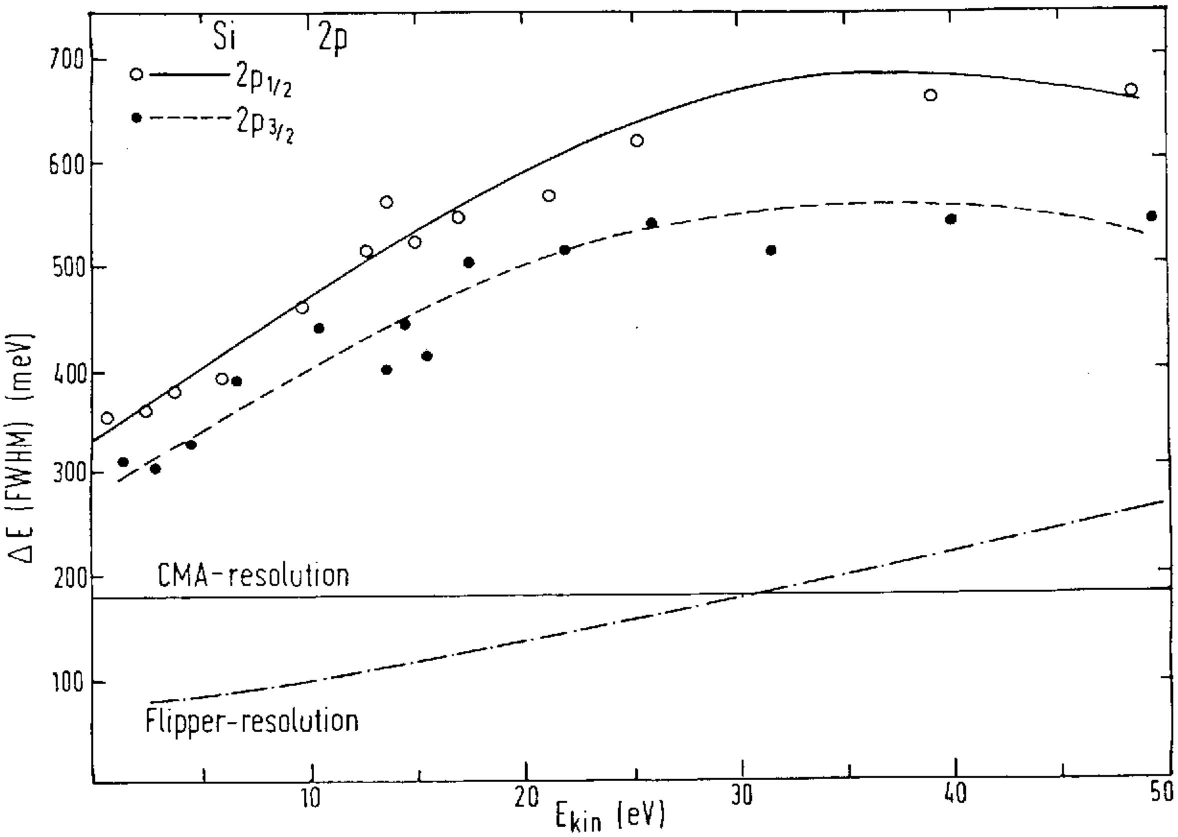
Si 2p
$2p_{1/2}$
$2p_{3/2}$
700
600
500
400
300
200
100
ΔE (FWHM) (meV)
CMA-resolution
Flipper-resolution
10
20
30
40
50
E_{kin} (eV)

Fig. 6 a

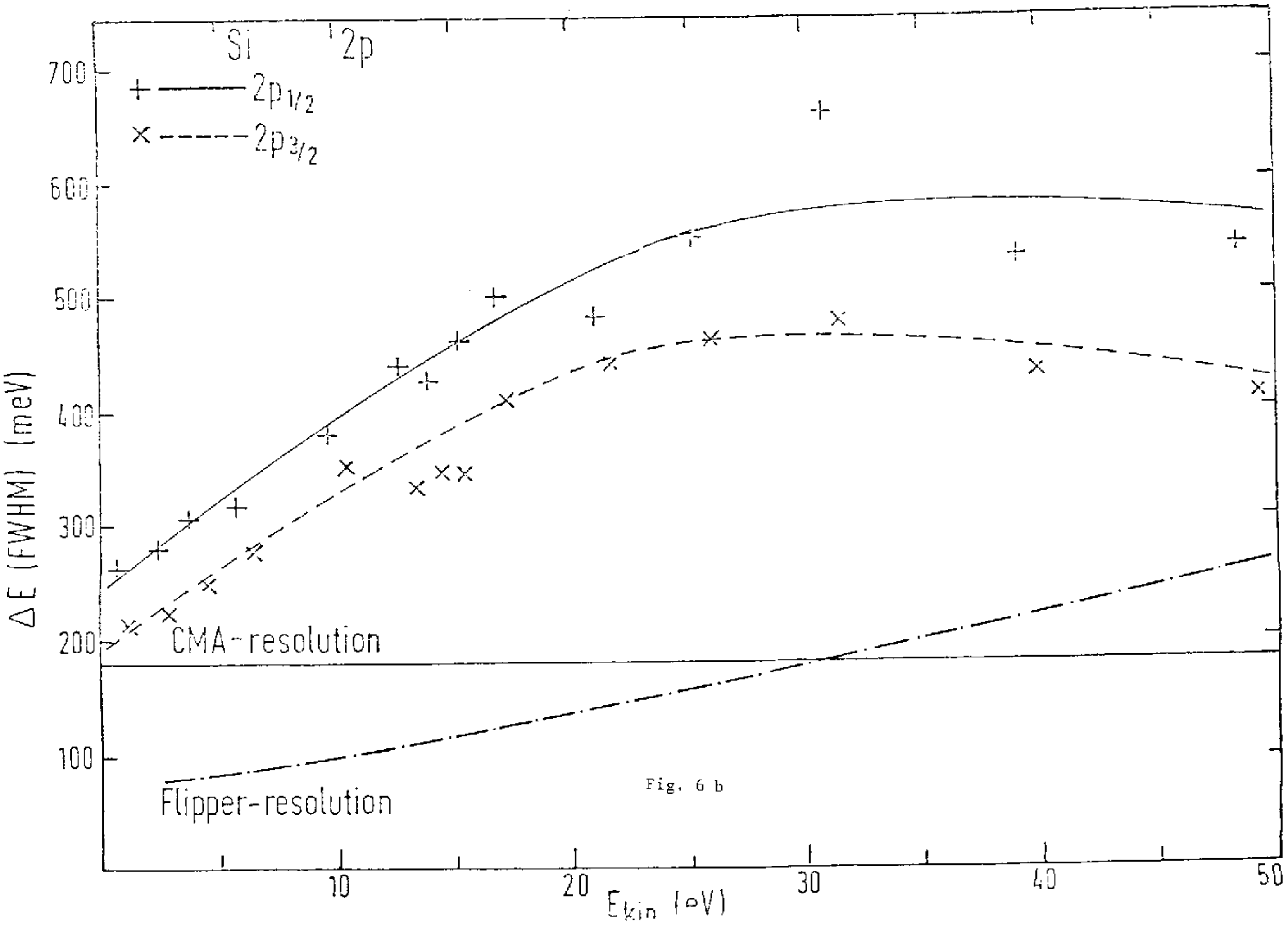
Si 2p
$2p_{1/2}$
$2p_{3/2}$
700
600
500
400
300
200
100
ΔE (FWHM) (meV)
CMA-resolution
Flipper-resolution
10
20
30
40
50
E_{kin} (eV)

Fig. 6 b

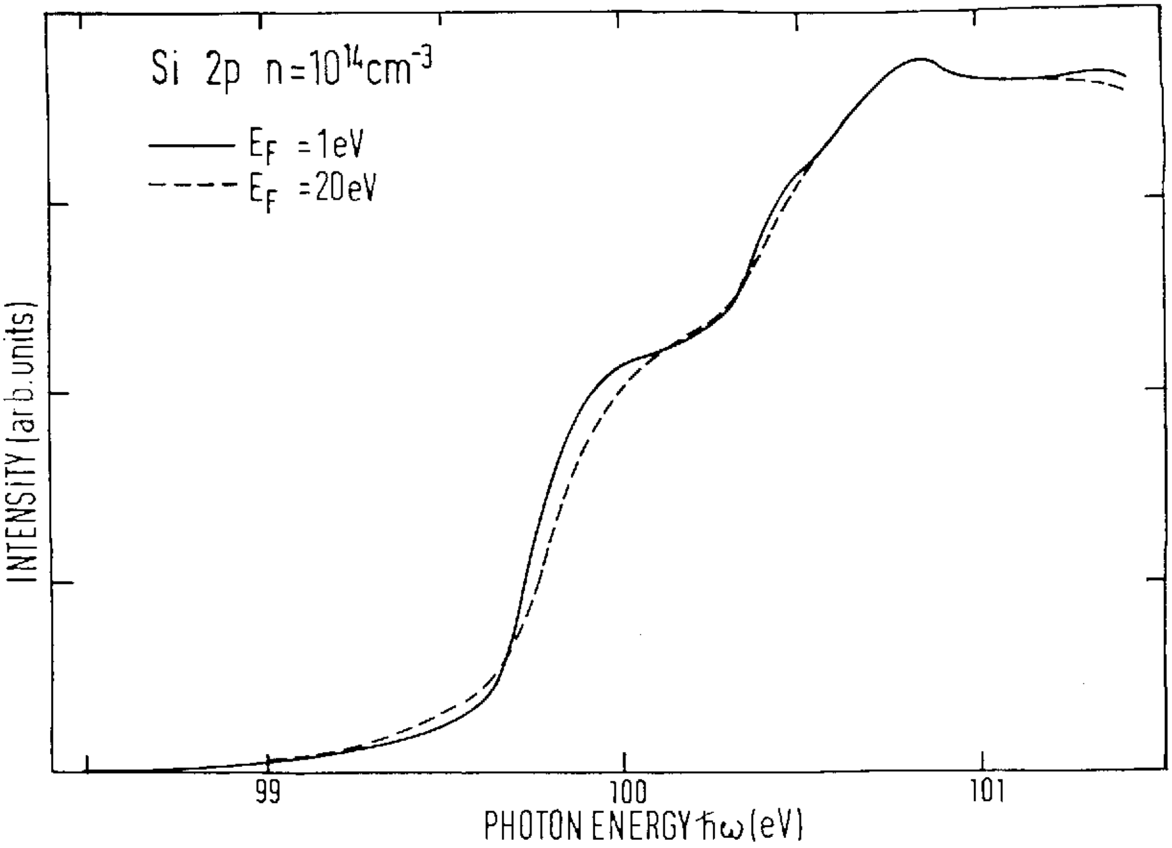
Si 2p $n = 10^{14} cm^{-3}$
E_F = 1eV
E_F = 20eV
INTENSITY (arb.units)
99
100
101
PHOTON ENERGY ħω (eV)

Fig. 7