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DIRECTION OBSERVATION OF "GAP STATES" IN c-Si AND a-Si:H BY SOFT X-RAY EMISSION

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RESUME Les spectres L_{23} de Si dans c-Si, a-Si et a-Si:H montrent une structure faible qui correspond aux états occupés dans l’écart énergétique. Leurs intensités et l’absence d’une modification de ces intensités après dopage par le B ou le P suggèrent que l’origine de ces états se trouve dans une zone de surface de séparation.

Abstract The L_{23} emission spectra of Si from c-Si, a-Si and a-Si:H show weak structures corresponding to filled states in the energy gap. Their intensities and the absence of change in this after doping strongly n- or p-type with B or P suggest that these are surface interface states.

INTRODUCTORY AND EXPERIMENTAL

Soft X-ray emission bands provide a direct representation of occupied valence state densities, albeit convoluted with both transition probabilities and core level broadening functions. Provided they are below the Fermi level, states lying in the energy gap in a semi-conductor will be filled and can then give rise to emission intensity immediately to the high energy side of the main valence band.

The UWA grazing incidence spectrometer currently uses a 1m radius concave grating ruled in gold with 2400 grooves per mm and a 1° blaze. At 85.5° angle of incidence and with 50μm slits the instrumental resolution in first order is 0.24Å which corresponds to 0.2eV for the Si-L_{23} band at a wavelength ~125Å. The spectra were produced by direct electron excitation in LN2 cooled samples in a cold-trapped high vacuum (typically < 5x10^{-8} torr). An electron beam of 1-2mA at 3.0kV was focussed in an area about 0.5x5.0mm (~80mA/cm²) and the estimated temperature of the emitting region is ~90K. The samples showed no visible signs of damage following 4-5 hour exposure to the beam.
Spectra were recorded from both nominally intrinsic polycrystal and intrinsic single crystal (2.5 × 10^{-3} \ \Omega \text{cm}) (c-Si), amorphous silicon (a-Si) prepared by in situ evaporation on to a LN$_2$ cooled copper target and from hydrogenated amorphous silicon prepared on copper mounting strips from a glow discharge in silane (SiH$_4$) as described by Haneman and Zhang\(^1\) (a-Si:H intrinsic and p- or n- doped).

It was possible to monitor the slow process of contamination under the action of the electron beam through the intensity of the C-K$_\alpha$ band which is emitted at 44.7\,Å (277\,eV). For polycrystal samples, scraping with a tungsten carbide knife \textit{in vacuo} reduced the C-K$_\alpha$ intensity to zero. For the single crystal and amorphous hydrogenated samples no in situ surface treatment was possible and the inevitable pickup of hydrocarbons during handling and initial pumpdown and later even in the clean vacuum conditions meant that the C-K$_\alpha$ intensity increased by a factor of 3-5 from the small initial value over a three hour observation period. In careful tests, successive scans were shown to be identical over a period of several hours (apart from a small overall intensity drop). In particular the intensity of the gap state emission relative to the main band is \textbf{unchanged} as time (and contamination) proceeds. Comparing the intensity from graphite targets with the measured intensity of C-K$_\alpha$ from the contaminant film we estimate a thickness of carbonaceous deposit of some 75-120\,Å at the end of a typical 3 hour run.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Gap state emission recorded for various samples. The data have been corrected in part for instrumental and core level widths. \(E_V\) indicates an extrapolation of the valence band.}
\end{figure}
Results and Discussion

We turn attention first to the gap state emission observed for c-Si, which is totally unexpected, and though less intense than for the amorphous samples has been established as a real feature. The number of states corresponding to an emission feature can be estimated by comparing the integrated intensity with that of the main band and assuming a single s-electron per atom contributing in the main Si-L$_{23}$ emission band.

The single crystal intrinsic silicon sample was cut from a Wacker Chemic float zone crystal sample of resistivity $2.3 \times 10^3 \Omega \text{cm}$, corresponding to about $2 \times 10^{12}$ n-type impurities cm$^{-3}$. i) The integrated intensity of emission (for c-Si) for the small peaks above the valence band edge relative to the main band is 0.06% which corresponds with at least $3 \times 10^{19}$ states cm$^{-3}$ and exceeds reasonable worst case O and C impurity concentrations by more than an order of magnitude. ii) Even if one assumes that the states in the gap are pure s-like, it is still highly improbable that their transition probability can be orders of magnitude higher than for valence band states, particularly as the bottom of the valence band is known to have considerable s-like character itself. iii) Although the valence states are extended in space and any postulated gap states are localised, any greater transition probability of the latter due to this cause is offset by the reduced probability of a core hole being created within their sphere, compared with extended valence states which can in principle "use" any available core hole.

The integrated intensity of gap state emission for c-Si is about 0.06% of that of the valence band and its peak height is about 1/60 that of the latter. Consider the emission from a single layer at the surface, of unspecified nature, compared with the average 800Å (400 layers) from which the total emission is observed$^2$. For similar bulk density ($5 \times 10^{22}$ cm$^{-3}$) and transition probabilities its integrated emission intensity would be $-1/400$ of the total or $-1/800$ if we take account of the depth dependence of ionisation by the incident electron beam$^2$. In order to account for the observed peak intensity in the gap emission, the width of the emitting states would have to be about 60/800 times that of the Si-L$_{23}$ band width of about 13eV, i.e. about 1eV, in agreement with the observations. We thus seek an origin in the surface region for a band of about 1eV width, located a few tenths of a volt above the valence band edge and having a peak state density about $1.2 \times 10^{22}$ cm$^{-3}$eV$^{-1}$ if it is a single layer. There are three possible sources, the surface oxide layer, the interface between silicon and the oxide and the interface between oxide and the surface contaminant layer. The contaminant hydrocarbon layer itself is not a candidate since it grows with time, as described above, whereas the peak in question remains constant in intensity relative to the main band. The oxide layer is a consequence of short exposure to air prior to insertion in the vacuum system and is 20-30Å thick with a large band gap and no known states close to the Fermi level. The silicon/silicon oxide interface usually has a low state density, orders of magnitude less than required here. This leaves the silicon oxide/contaminant
interface about which little is known and pending further information we presume that this is the origin of the observed emission. Since the contaminant layer has no particular structural match to the oxide it is feasible that the required high interface state density of order $10^{22} \text{ cm}^{-3}$ occurs and since the states are fairly localised the required band width of about 1eV also appears to be quite feasible.

We refer now to the even greater density of gap states observed with the various a-Si:H samples and the evaporated a-Si samples (not illustrated here). Similar emission is evident in the spectra of Wiech and Zöpf\textsuperscript{3}, Senemaud et al\textsuperscript{4,5} and Terekhov et al\textsuperscript{6} but these authors have not commented on the intensity anomaly. All these hydrogenated materials are believed to have a large band gap with low gap state density, about $10^{16}-10^{17} \text{cm}^{-3} \text{ eV}^{-1}$ and thus cannot account for the observed peak heights in the gap region, which are some five times more intense than for c-Si. For a band of width 1eV one would thus require a density of about $1.5 \times 10^{20}$ states cm\textsuperscript{-3} if distributed uniformly over the emitting region or $6 \times 10^{22} \text{ cm}^{-3}$ if in an interface layer in the surface region. Since the normal gap state density is insufficient by orders of magnitude, we must again postulate interface states as the source, namely states between the film and the contaminant layer. Weight is lent to this postulate, or at least to a surface origin, by the observation that for both crystalline and amorphous material the intensity of the gap state emission relative to the main band increases if the excitation voltage is reduced to 1.0kV, favoring emission from the surface region. In the case of a-Si:H, note that the gap state emission intensity is similar for both intrinsic and heavily doped n-type (1% PH\textsubscript{3} in SiH\textsubscript{4}) films and differs slightly for the p-film (0.75% B\textsubscript{2}H\textsubscript{6} in SiH\textsubscript{4}). If the gap state emission was from the bulk material then n-doping, which raises the Fermi level, should enhance the emission by increasing the filled population while p-doping should have the opposite effect. Such is not the case.

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