Auger Lineshape Analysis of Disorder and Rehydrogenation Induced Changes in the Electronic Structure of Silicon Surfaces*

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Abstract

X-ray excited Si $L_{23}VV$ spectra have been measured for both disordered crystalline silicon and chemical vapour deposited amorphous silicon. A method, based on the Simplex algorithm, has been applied to enable the Si $L_{23}VV$ peak to be decomposed into its $L_{23}M_1M_{23}$, $L_{23}M_{23}M_{23}$ and localised two-hole components. Changes in the relative amounts of the $L_{23}VV$ components have been compared with changes upon hydrogenation by direct hydrogen ion bombardment for both the disordered c-Si and a-Si samples. Recent published results related to monitoring the effects of disorder and then hydrogenation on silicon surfaces using the Si $L_{23}VV$ Auger lineshape are reviewed and show good agreement with the results obtained. In agreement with others it is concluded that the hydrogen decreases the localised defect states in the bandgap and creates new states in the valence band. It is shown that the effect is more pronounced in disordered a-Si than in disordered c-Si. Hydrogenation of this sort is effective in improving the electrical properties of the films, especially for chemical vapour deposition films.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) has long been recognised as a promising material for photovoltaic devices (Zwiebel and Ullal 1989). It is also being used in an increasing number of other semiconductor devices and there is lively interest in developing other applications of a-Si:H films (Overhof and Thomas 1989). In these applications, surface and interface properties of the semiconductor often play an important role in determining the performance of the device.

It has been stated that the lack of long range order in a-Si:H, and the presence of defects in the structure are reflected in the presence of a tail of localised states extending from the top of the valence band (VB) into the energy gap (Madden and Hjalmerson 1982). It is also believed that the presence of the hydrogen in amorphous silicon causes a decrease in the defect states at the top of the VB due to its ability to terminate the dangling bonds in the a-Si structure (Madden 1983*a*).

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With the advances in material preparation and characterisation technologies, supported by ultra-high vacuum techniques and computerised measurement systems over the last 10 to 15 years, remarkable progress has been made in the study of disordered materials, both theoretically and experimentally. One such useful technique has been Auger electron spectroscopy (AES). Since AES is sensitive to the variation of the local atomic charge density across the VB (Jennison 1978, 1982; Feibelman *et al.* 1978; Feibelman and McGuire 1978) it is a useful technique for characterising the defect states found near the valence band maxima due to the dangling bonds in a-Si:H.

Brockman and Russell (1980) have shown that experimental Si $L_1L_{23}V$ and $L_{23}VV$ Auger spectra, treated using numerical debroadening and deconvolution, can be used as an indication of the valence band density of states (VBDOS) for the surface. In the last five to ten years Auger lineshape analysis (ALA) of this sort has been used to correlate the electronic properties of a-Si:H, primarily the valence band and bandgap DOS, to its structure (Madden and Hjalmerson 1982; Madden 1983*b*). This has included studies of the effect of both disordering (Morgan and Ryborg 1980; Madden and Hjalmerson 1982) and hydrogenation (Madden 1983*a*, 1983*b*; Nelson *et al.* 1986; Burnham *et al.* 1987) on the lineshapes of the Si $L_1L_{23}V$ and Si $L_{23}VV$ lines and therefore the VBDOS. Most of this work has been performed on disordered c-Si (Feibelman and McGuire 1978; Madden and Hjalmerson 1982; Madden 1984) or in-situ RF sputtered a-Si (Zemek *et al.* 1980), with one or two results reported for glow discharge a-Si:H (Nelson *et al.* 1986; Burnham *et al.* 1987). To our knowledge no work has been reported for chemical vapour deposition (CVD) a-Si.
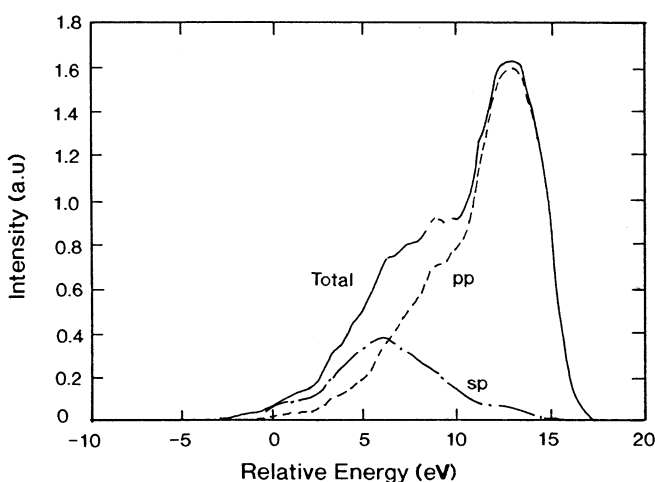

Fig. 1. Jennison's (1978) theoretical lineshape for the Si $L_{23}VV$ Auger transition.

Most of the work done recently, however, has used ALA of the Si $L_{23}VV$ band as the means of investigating the local chemical environment and the VBDOS in hydrogenated amorphous silicon (Madden 1981*a*, 1981*b*, 1984; Madden and Hjalmerson 1982; Zajak and Bader 1982; Clemens 1984). Considerable theoretical work has been done to define and characterise the individual components (ss,sp and pp) of the Si $L_{23}VV$ Auger transition (Feibelman *et al.* 1978; Feibelman and McGuire 1978). These have shown that the $L_{23}VV$

line reflects the VBDOS and is principally the self-convolution of the p-like contributions to this DOS which generates the LVV lineshape (Houston *et al.* 1977; Jennison 1978; Feibelman *et al.* 1978; Feibelman and McGuire 1978; Allie *et al.* 1980; Kunjunny and Ferry 1980, 1981). Since the effects of hydrogenation of a-Si manifest themselves mainly in the magnitude of the sp ($L_{23}M_1M_{23}$) component relative to the dominant pp ($L_{23}M_{23}M_{23}$) components in the Si L_{23}VV transition, the Auger process has been shown to be useful for monitoring in a semi-quantitative way the effects of the hydrogenation process (Nelson *et al.* 1986; Burnham *et al.* 1987). In this paper we also report results of measured X-ray excited Si L_{23}VV spectra for disordered crystalline material. This includes the results of hydrogenation by direct ion bombardment with hydrogen ion beams to observe the changes in the L_{23}VV lineshape due to hydrogen incorporation, similar to other authors (Madden 1983*a*; Nelson *et al.* 1986; Burnham *et al.* 1987). New results are presented for disordered and hydrogentated CVD a-Si samples. The L_{23}VV transition peak was decomposed into its sp ($L_{23}M_1M_{23}$), pp ($L_{23}M_{23}M_{23}$) and two-hole components using a method based on the Simplex algorithm. The Si L_{23}VV peaks were curve fitted with the individual Auger transitions (sp,pp and L2H) using Jennison's (1978) theoretical lineshape, as shown in Fig. 1. Changes in the relative amounts of the L_{23}VV components are compared for both the disordered c-Si and disordered CVD a-Si samples after hydrogenation. These were shown to be comparable with previously published theories and experimental results.

2. Experimental

The disordered (amorphised) crystalline silicon samples were prepared by bombarding n-type Si(111) substrates (resistivity 0·5 to 4 ohm cm^{-1}) with 10 keV argon ions for about 15 min. With argon ion doses as large as this the surface was amorphous after ion bombardment according to the specifications of Muller and Kalbitzer (1980). The CVD samples were prepared using atmospheric pressure CVD following the method outlined by Ellis and Gordon (1983). They were prepared on stainless steel substrates at a temperature of ~650°C using a deposition system described earlier (Jennings *et al.* 1988), and then transferred to the UHV analysis system. These samples were then bombarded using argon ions in the same way as the crystalline samples to remove any atmospheric contamination. Hydrogenation of the disordered surfaces, both the c-Si and CVD a-Si samples, was achieved by a method similar to that of Madden (1983*a*) and others (Nelson *et al.* 1986; Burnham *et al.* 1987). An ion gun was used to bombard the surfaces with 3 keV hydrogen ions. Fluences were of the order of 4×10^{22} cm^{-2}.

Auger analysis was performed in a Vacuum Generators ESCA Lab system with a base pressure of 10^{-11} Torr (1 Torr $\equiv$ 133 Pa). AES data were obtained with a MgKα X-ray beam in the integral $N(E)$ mode from a hemispherical (XPS) analyser. These spectra were then corrected for loss and background effects and smoothed using the Savitsky–Golay 9 point algorithm.

Curve fitting of the pp, sp and localised two-hole components of the Si L_{23}VV spectra was accomplished by using Simplex fits (Kojima and Kurahashi 1987) of three gaussian asymmetric (Jurs 1986) peaks to the corrected Auger spectra. The fitting program optimised the values of the parameters by minimising the

value of the sum of chi-squared over all the data points and could fit up to four separate peaks, each with its own asymmetry and half-width (Thurgate and Erickson 1990). In the same way as Nelson, Burnham and co-workers, Jennison's (1978) theoretical Si LVV Auger line shape was used as a model for the curve fit, such that the pp component was the best fit to the sum of two gaussians, while the sp and the localised two-hole components were the best fits to single gaussians. These results are reported below.
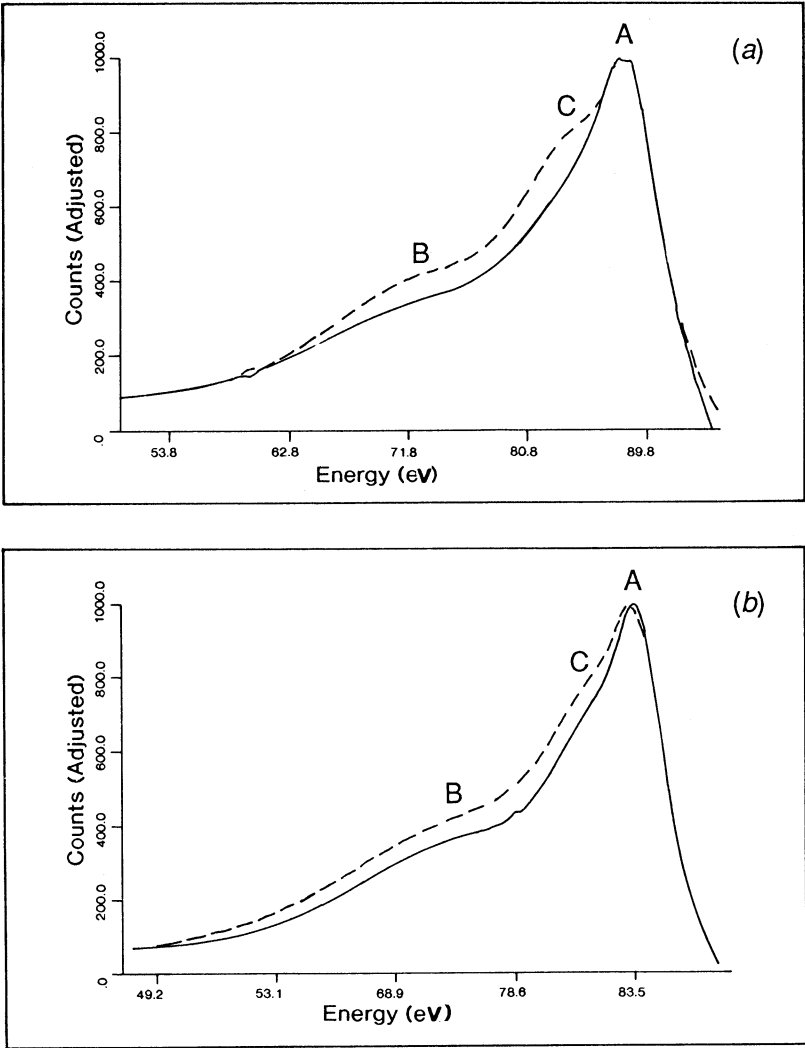

Fig. 2. Loss-corrected normalised Si L_{23}VV spectra for disordered (solid curve) and rehydrogenated (dashed curve) samples: (*a*) c-Si and (*b*) a-Si. Features A, B and C are discussed in the text.

3. Results and Discussion

The Si L_{23}VV spectra for the disordered and rehydrogenated c-Si (111) surfaces are shown in Fig. 2*a*. For comparison the spectra are presented in

loss-corrected $N(E)$ mode, and after normalisation, in the same way as other authors (Madden 1983a; Nelson et al. 1986; Burnham et al. 1987). Fig. 2b presents the Si L_{23}VV spectra for the disordered and rehydrogenated CVD a-Si films. Hydrogen induced changes in both of these are labelled and can be described as: A, a shift in the high energy edge of the spectral line; B, a broadening of the main Auger peak on the low energy side; and C, a distinct increase in the shoulder at the low energy end of the spectral line.

Following previous interpretations of the hydrogen induced spectral changes (Madden 1981a; Madden et al. 1982; Zajak and Bader 1982; Madden and Hjalmerson 1982; Nelson et al. 1986; Burnham et al. 1987), feature A, which is related to the pp ($L_{23}M_{23}M_{23}$) component of the Si L_{23}VV line, results from a decrease of states at the top of the VB due to termination of dangling bonds by the hydrogen in the a-Si structure. Feature B results from the establishment of new electron energy levels associated with Si-H bonding. This feature is related to an increase of the sp ($L_{23}M_1M_{23}$) component relative to the dominant pp ($L_{23}M_{23}M_{23}$) component of the Si L_{23}VV line due to the increased localisation of the silicon 3s-like band with increasing hydrogenation (Zajak and Bader 1982). Feature C is interpreted as being due to a correlated two-hole Auger final state (Madden and Hjalmerson 1982; Madden et al. 1982) in the VB. This region of the Si L_{23}VV line also contains the contribution from the ss component and enhancement of this feature with increasing hydrogen concentration may be due to Auger matrix element effects (Madden et al. 1982), since the theoretical ss convoluted surface DOS shows minimal change with increasing hydrogen concentration.

Each of these features was resolved into individual components so as to quantify the effects of hydrogenation, in a similar way to that of Nelson, Burnham and co-workers. The decoupled spectra are shown in Fig. 3. The individual components were defined as such by fitting their sums as accurately as possible to the actual experimental data. Fig. 3 inserts show the sum of all bands over the original data.

Areas under the pp, sp and localised two hole (L2H) components were then calculated, as shown in Table 1. The first point to note is the general decrease in the pp component compared with the total Si L_{23}VV line area with hydrogenation for both the disordered crystalline and disordered CVD samples. This relative decrease is more pronounced for the CVD sample than for the c-Si sample. Following the arguments of Madden and Hjalmerson (1982) and Nelson, Burnham and co-workers (1986, 1987), this trend suggests that there is a decrease in defect states (dangling bonds) in the VB with hydrogenation. Our results also suggest that for the same hydrogenation treatment more defect states are removed in the CVD material than in the c-Si. This suggests that hydrogenation has a greater effect on the CVD than the c-Si material. It appears that the CVD material is intrinsically different to the c-Si even after disordering. Secondly it can be seen that there is a general increase in both the sp and L2H components relative to the pp component with increased hydrogenation. Again the effect is greater for the CVD sample. In agreement with the interpretation of Nelson, Burnham and co-workers the fact that the ratio of the sp component to the pp component is increasing with hydrogenation confirms that new energy levels are being established in
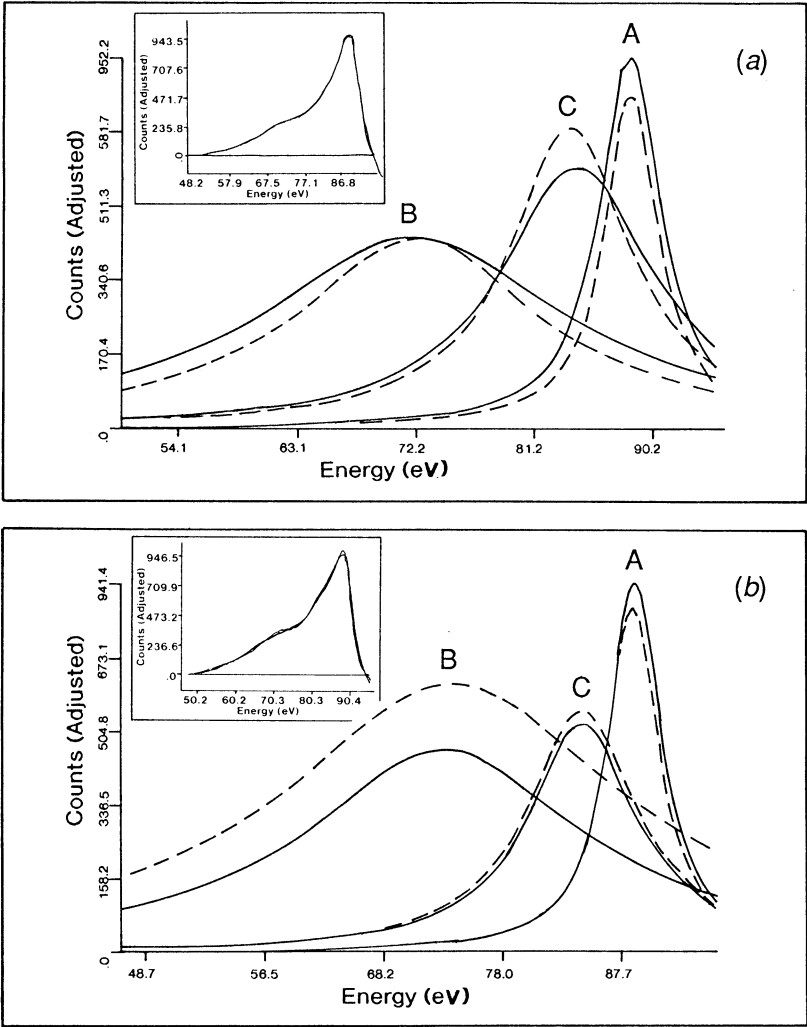
Fig. 3. Comparison of individual components of the Si L$_{23}$VV spectra for disordered (solid curve) and hydrogenated (dashed curve) samples: (*a*) c-Si and (*b*) a-Si. Insets show the sum of all bands over the original data. Features A, B and C are discussed in the text.

Table 1.   Ratio of integrated Auger areas of the pp, sp and L2H components of the Si L$_{23}$VV line in disordered c-Si and a-Si samples

Sample	pp/total	sp/total	L2H/total	sp/pp	L2H/pp
c-Si disordered	0·21	0·44	0·35	2·10	1·63
c-Si rehydrogenated	0·19	0·42	0·38	2·19	1·99
a-Si disordered	0·23	0·50	0·27	2·20	1·19
a-Si rehydrogenated	0·16	0·61	0·23	3·79	1·45

the VB due to Si-H bonding. As with the pp/total ratio, this effect especially in the sp/pp ratio is greatly enhanced in the CVD sample. Again it would appear from our results that the rehydrogenation technique used is more effective in satisfying the dangling bonds and establishing new energy levels in the VB in disorderd CVD a-Si material. Whether this is true of the as deposited CVD a-Si material is not known. This will be the focus of further experiments.

4. Conclusions

Detailed line-shape analysis of the X-ray excited $L_{23}VV$ Auger transition has been performed on a-Si:H. These results show that this technique is useful for obtaining information on the VBDOS and bonding effects in a-Si:H. A method based on the Simplex algorithm has been successfully applied to enable the Si $L_{23}VV$ peak to be decomposed into its $L_{23}M_1M_{23}$, $L_{23}M_{23}M_{23}$ and localised two-hole components. Changes in the relative amounts of the $L_{23}VV$ components on hydrogenation have been compared with previously published theoretical and experimental results. Specifically:

(1) In line with others (Madden and Hjalmerson 1982; Nelson *et al.* 1986; Burnham *et al.* 1987), changes in the Si $L_{23}VV$ lineshape suggest that hydrogenation decreases the defect states due to dangling bonds at the top of the VB in disordered c-Si and causes the appearance of new electron energy levels in the VB due to Si–H bonding. Our results suggest that this is also true for disordered CVD a-Si with even larger changes being observed.

(2) The method of hydrogen ion gun hydrogenation has been shown to have a greater effect on disordered CVD a-Si samples than on disordered c-Si. This suggests that it is more effective in satisfying the inherent dangling bonds and establishing new energy levels in the VB for CVD a-Si, compared with disordered c-Si (i.e. the CVD material is intrinsically different to c-Si even after disordering).

Acknowledgments

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