Determination of Band Discontinuity in Amorphous Semiconductor Heterojunctions

Tsukasa HAYASHI, Seiichi MIYAZAKI and Masataka HIROSE
Department of Electrical Engineering, Hiroshima University
Higashihiroshima 724, Japan

A new method of determining the band offset in semiconductor heterojunctions has been developed. The valence band spectra for heterojunctions consisting of ultra thin stoichiometric amorphous silicon nitride (a-Si$_3$N$_4$:H) or silicon carbide (a-Si$_{1-x}$C$_x$:H) grown on hydrogenated amorphous silicon (a-Si:H) have been measured by using x-ray photoelectron spectroscopy. The valence band discontinuities in a-Si$_3$N$_4$:H/a-Si:H and a-Si$_{1-x}$C$_x$:H/a-Si:H systems have been determined to be 1.7 eV and 0.1 eV (x=0.23), respectively.

1. Introduction

Characterization of semiconductor heterojunction interfaces in solid state devices is getting more and more important for designing and fabricating novel device structures. Recently the existence of quantized states in a-Si:H well layer has been directly demonstrated by the resonant tunneling through a-Si:H/a-Si$_3$N$_4$:H double barrier structures.[1] The quantum mechanical effects in amorphous semiconductor multilayers have been utilized for improving device performance.[2-4] Also, p-type a-Si$_{1-x}$C$_x$:H/undoped a-Si:H heterojunctions are now widely used for high efficiency thin film solar cells.[5] Quantitative knowledge on the band offset of heterojunctions has currently been obtained by using internal photoemission[6] or valence band spectra under VUV or SOR excitation[7,8] although the results are not necessarily consistent with each other. We have used x-ray photoelectron spectroscopy (XPS) for the exact measurement of the valence band discontinuity. This new technique employs high S/N ratio measurements of the valence band spectrum for a very thin heterojunction structure. Since the spectrum can be deconvoluted into the signals from the corresponding heterojunction materials, the band offset is directly determined.

2. Experimental

2.1 Sample Preparation

Amorphous silicon nitride (10 - 40 A thick)/a-Si:H (500 A) and a-Si$_{1-x}$C$_x$:H (10 - 40 A)/a-Si:H (500 A) heterojunction structures were fabricated on c-Si(100) substrates by an rf glow discharge technique. Monosilane diluted to 10.2% in H$_2$ was used for a-Si:H deposition and SiH$_4$(10.2% in H$_2$) +NH$_3$(100%) with a molar fraction of [NH$_3$]/[SiH$_4$]=10 for a-Si$_3$N$_4$:H growth, while in a-Si$_{1-x}$C$_x$:H deposition SiH$_4$(10.2% in H$_2$)+CH$_4$(100%) gas mixtures with molar fractions of [CH$_4$]/[SiH$_4$] =5 - 20 were utilized. During the respective layer growth, substrate temperature, rf power and gas pressure were maintained at 250°C, 1 - 4W and 0.18 - 0.20 Torr, respectively.

Uniform ultra thin films with desired chemical compositions and abrupt heterojunction interfaces were deposited by precise control of the deposition sequence as reported elsewhere.[9]

2.2 Spectrum Analysis

An XPS system (Shimadzu ESCA 750H) used in the present study is equipped with a personal computer which enables us to make repetitional measurements of the core level and valence band spectra. Si_{2p}, N_{1s} and C_{1s} core level spectra were measured to characterize the chemical structure of the heterojunction interfaces and to calculate the thickness of a-Si_3N_4:H or a-$Si_{1-x}C_x$:H. Special care was taken for eliminating charge-up of samples and the binding energy was calibrated by the core level signals of Si_{2p} from a-Si:H and Au_{4f} from a thin deposit on the surface. Spectral noise was reduced by adaptive smoothing of XPS data. The valence band spectrum of a thin heterojunction structure must be a convoluted spectrum of the two constituent

materials. In other words, the measured spectrum can be deconvoluted to the two spectra originating in both of the heterojunction materials. When the both spectral shapes are known from a separate measurement of the respective material, the valence band discontinuity can be determined as a difference of the band edge energies of the deconvoluted spectra.

3. Results and Discussion

3.1 a-Si_3N_4:H/a-Si:H Heterojunction

A typical valence band spectrum of 20 Å thick a-Si_3N_4:H on a-Si:H is displayed in Fig. 1 together with the deconvoluted spectra. A thin gold layer was evaporated onto the heterojunction sample after the valence band measurement. The energy separation between the $Au4f_{7/2}$ signal (83.8 eV) and the Si_{2p} peak (99.5 eV) from the underlying a-Si:H was used for the binding energy calibration. The valence band edges for a-Si_3N_4:H and a-Si:H measured as a function of a-Si_3N_4:H film thickness are shown in Fig. 2. The result indicates that
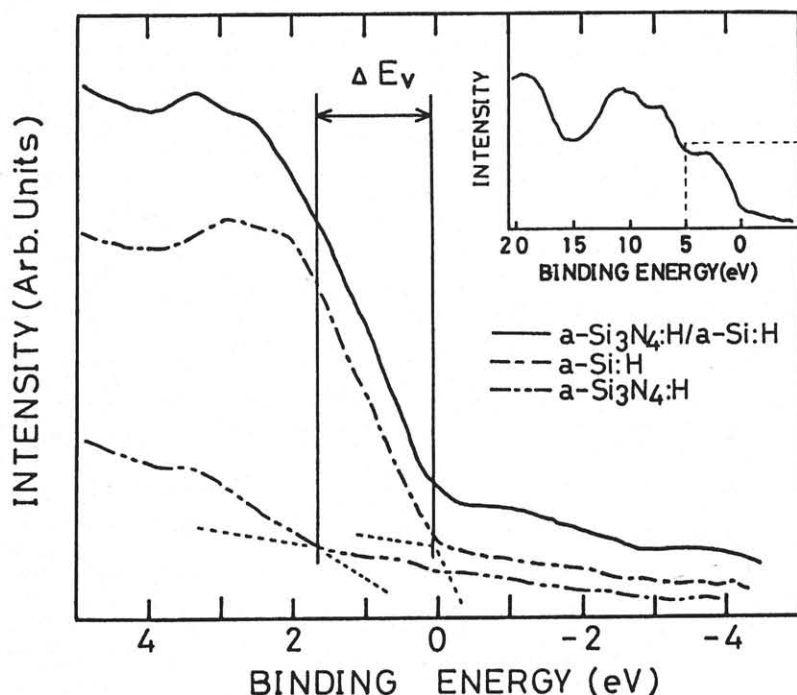

Fig.1 Valence band spectrum from an a-Si_3N_4:H (20 Å)/a-Si:H heterojunction and the deconvoluted spectra.

the valence band offset ΔEv is 1.7 eV regardless of a-Si$_3$N$_4$:H film thicknesses. This value agrees well with that estimated by internal photoemission measurements for the same system.[1] By taking into account the optical band gaps of a-Si$_3$N$_4$:H (5.2 eV) and a-Si:H (1.8 eV), the band diagram of the heterojunction can easily be drawn.

3.2 a-Si$_{1-x}$C$_x$:H/a-Si:H Heterojunctions

The valence band discontinuities in a-Si$_{1-x}$C$_x$:H/a-Si:H systems were determined in the carbon compositional range 0.23≤x≤0.53.

The valence band spectrum for a 20 A thick a-Si$_{1-x}$C$_x$:H (x=0.23) on a-Si:H is shown in Fig. 3. Note that a residual signal appears in the energy range 1 - 5 eV after deconvolution. This might arise from states in the interface. The band offset is again independent of a-Si$_{1-x}$C$_x$:H layer thicknesses. Figure 4 represents the extent of the valence band discontinuity measured as a function of x. Amorphous silicon carbide with x=0.23 is used as a window layer of a-Si:H solar cells. It is clear that the valence band offset at an a-

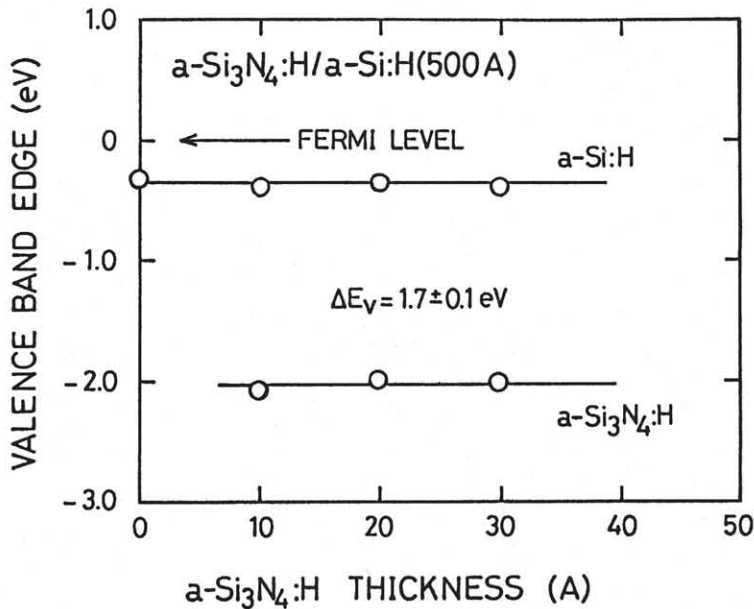Fig.2 Valence band discontinuity for an a-Si$_3$N$_4$:H/a-Si:H system as a function of a-Si$_3$N$_4$:H film thickness.
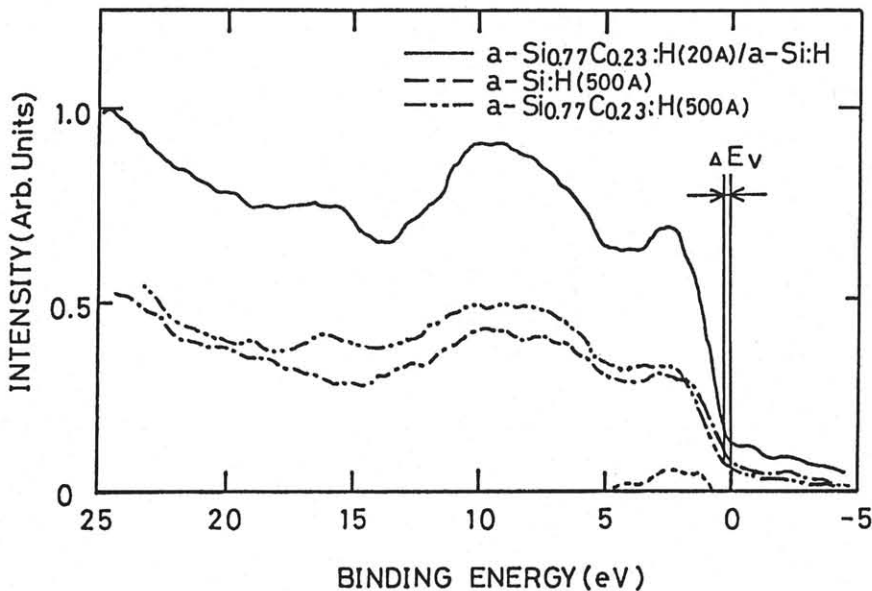
Fig.3 Valence band spectrum from an a-Si$_{0.77}$C$_{0.23}$:H/a-Si:H system and the deconvoluted spectra.

$Si_{0.77}C_{0.23}$:H/a-Si:H heterojunction is estimated to be 0.1 eV which is significantly larger than the thermal energy of photogenerated holes. This implies that the valence band offset at the a-$Si_{0.77}C_{0.23}$:H/a-Si:H heterojunction might act as a barrier for hole current transport in a-Si:H solar cells with a silicon carbide window.

In conclusion, it is demonstrated that the valence band spectra measured by XPS can yield the band offset of semiconductor heterojunctions.
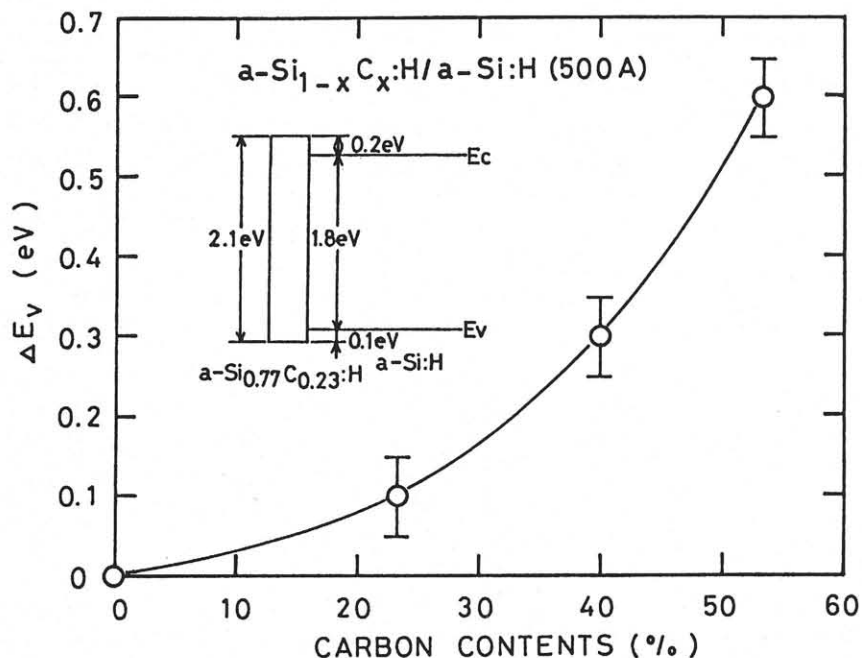

Fig.4 Valence band offset of an a-$Si_{1-x}C_x$:H/a-Si:H system as a function of carbon content.

References

1) S. Miyazaki, Y. Ihara, and M. Hirose; Extended Abstracts of the 6th Intern. Conf. on solid State Devices and Materials (Tokyo, 1986) p. 675.
2) S. Miyazaki, N. Murayama, and M. Hirose; Extended Abstracts of the 17th Conference on Solid State Devices and Materials (Tokyo, 1985) p. 107.
3) H. Tarui, T. Matsuyama, S. Tsuda, Y. Hishikawa, T. Takahama, S. Nakayama, N. Nakamura, T. Fukatsu, S. Nakano, M. Onishi, and Y. Kuwano; Extended Abstracts of the 6th Intern. Conf. on Solid State Devices and Materials (Tokyo, 1986) p. 687.
4) M. Tsukude, S. Akamatsu, S. Miyazaki, and M. Hirose; Jpn. J. Appl. Phys., 26 (1987) L111.
5) Y. Hamakawa, and Y. Tawada; Int. J. Solar Energy 1 (1982) p. 125.
6) M. Cuniot, and Y. Marfaing; J. Non-Cryst. Solids 77 & 78 (1985) 987.
7) C. Coluzza, G. Fortunato, C. Quaresima, M. Capozi, and P. Perfetti; J. Non-Cryst. Solids 77 & 78 (1985) 999.
8) F. Evangelisti, P. Fiorini, and C. Giovannella; Appl. Phys. Lett. 44 (1984) 764.
9) M. Hirose, N. Murayama, S. Miyazaki, and Y. Ihara; Materials Research Sosiety Symp. Proc. 70 (1986) p. 405.