Photothermal Modulation Spectroscopy of Multilayered Structures of Amorphous Silicon and Amorphous Silicon Carbide

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Thermal modulation spectroscopy based on a photothermal process has been applied to hydrogenated amorphous silicon (*a*-Si:H)–silicon carbide (*a*-SiC:H) multilayered structures. The temperature derivative of the absorption spectrum drastically changes from a linear to a staircase form with decreasing *a*-Si:H well-layer thickness below 50 Å. This result suggests that three-dimensional parabolic band transition is turned into subband transitions in the *a*-Si:H quantum well.

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The band structure of amorphous semiconductor multilayers is of fundamental interest for the understanding of quantization effects in disordered systems. The most direct way to study the band structure is to measure the optical absorption spectrum. The observed absorption spectrum of the multilayered structures,[1] however, does not exhibit any features distinguishable from that of the bulk materials, and hence provides us no definitive information about quantized band structures. The structureless absorption spectrum seems to come essentially from optical transition processes involving a relaxed momentum selection rule in amorphous materials, which tends to reduce structures in the spectrum reflecting the quantized density of states. It is then required to introduce experimental approaches with high detection sensitivity for extraction of these structures from the unresolved absorption spectrum. Such extreme sensitivity is considered to be obtained in optical modulation techniques.[2]

In this Letter, we report on the use of photothermal modulation (PTM) spectroscopy to study interband optical transitions in multilayered structures composed of hydrogenated amorphous silicon (*a*-Si:H) and silicon carbide (*a*-SiC:H). PTM spectroscopy is a conventional thermal modulation spectroscopy[2] in which the temperature of the sample is modulated by heat produced by light absorption. Since the band gap shifts with varying temperature, one can consequently obtain the gap derivative of the absorption spectrum by measuring the thermally induced change in absorption. The PTM spectra measured on the *a*-Si:H–*a*-SiC:H multilayered structures drastically changes from a linear to a staircase form with decreasing *a*-Si:H well layer thickness below 50 Å. The observation indicates that the three-dimensional (3D) parabolic band transition is turned into transitions between quantized band states (subband states) in the *a*-Si:H quantum well.

The multilayered structures were prepared on glass substrate by rf plasma chemical vapor deposition with use of a 1:9 SiH_4-H_2 gas mixture for the *a*-Si:H layers and 1:13:126 SiH_4-CH_4-H_2 gas mixture for *a*-SiC:H layers. Each layer was formed in a separate chamber with interruption on the plasma. The thicknesses of the sublayers were determined by the deposition time and the deposition rates for the thick films. The *a*-Si:H well-layer thickness was varied from 20 to 1000 Å while keeping the total well-layer thickness at 3000 Å, and the *a*-SiC:H barrier-layer thickness was fixed at 100 Å to avoid interlayer carrier tunneling. The optical band gaps were 1.75 and 2.80 eV for *a*-Si:H and *a*-SiC:H, respectively, which were determined from the optical-absorption spectra of identical thick films following a Tauc plot. The band discontinuities were estimated to be 0.80 eV for the conduction band and 0.25 eV for the valence band from the results of ultraviolet photoelectron emission measurement by use of a Fowler plot.[3,4] An identical offset energy of the valence-band edge has been deduced from the deconvolution procedure for an x-ray photoelectron spectrum measured on *a*-SiC:H-*a*-Si:H heterostructure by Hirose.[5]

In the PTM experiment, two light sources are used: a pump for heat generation and a probe for measurement of the induced change in transmission. The pump light from an Ar^+-ion laser (488 nm) with an intensity of 1 W/cm^2 was mechanically chopped at 5 Hz. White light with an intensity of 5 mW/cm^2 was used as the probe light, and the transmitted light was dispersed by a monochromator. The transmission I and its modulated component ΔT were detected by a photomultiplier and a lock-in amplifier. The temperature derivative of the absorption coefficient is proportional to $-\Delta T/T$ over the spectral region of photon energy above the absorption edge of the *a*-Si:H sample, as indicated by Pfost *et al.*[6] The samples were held in a cryostat, and measurements were performed at a temperature of 100 K to minimize thermal broadening of the PTM spectrum.

Before going into the description of the experimental result, we will briefly discuss what kind of absorption spectrum is expected for the interband transition in both bulk and quantum wells. The absorption coefficient α associated with the transition between 3D parabolic bands

in amorphous semiconductors is expressed by

$$\hbar\omega\alpha \propto (\hbar\omega - E_0)^2 U(\hbar\omega - E_0), \quad (1)$$

within the context of the model assuming a completely relaxed selection rule for the wave vector $\mathbf{k}$ and a constant momentum matrix element.[7] Here E_0 denotes the Tauc optical gap, $\hbar\omega$ the photon energy, and $U(E)$ a step function. If the dipole matrix element is assumed to be constant, the left-hand side of the relation (1) is replaced by $\alpha/\hbar\omega$.[7] However, this does not essentially alter the conclusions reached in the following discussion.

In an amorphous semiconductor multilayered structure, suppose that the well-layer thickness is reduced to less than the carrier mean free path so that the carrier system in the well layer enters into the quantum regime. Quantization of the wave function in the direction perpendicular to the well-layer plane brings about the subband states of constant density $m^*/\pi\hbar^2 L_W$. The quantity m^* denotes the effective mass, and L_W the thickness of the well layer. Each subband is labeled by the confined-state quantum number $n(=1,2,3,\ldots)$. Transitions between subband states should obey an approximate selection rule for confined states ($\Delta n = 0$), whereas the k-selection rule in the direction parallel to the well plane remains relaxed.[8,9] Therefore, the absorption coefficient for transitions between subband states will follow

$$\hbar\omega\alpha \propto \sum_n (\hbar\omega - E_n) U(\hbar\omega - E_n), \quad (2)$$

$$n = 1,2,3,\ldots,$$

where E_n denotes energy separation between the nth subband edges in the conduction and valence bands.

In some previous experiments, optical-absorption spectra of multilayered structures were discussed in accordance with the Tauc plot as is normally done in the bulk materials.[1] This may lead to a misunderstanding of the band-edge structure, as is easily recognized by the comparison of expressions (1) and (2). In fact, the absorption spectra of the present multilayered structures, in which the well-layer thickness is less than 50 Å, show the behavior expected from Eq. (2) rather than Eq. (1), although they are not clearly identified.

The difference between the spectral shapes for the bulk and quantum wells appears to be more distinguishable in their derivatives, which correspond to the PTM spectrum:

$$S \equiv -\Delta T/T \propto \partial\alpha/\partial\theta$$

$$= \sum_m (\partial\alpha/\partial E_m)(\partial E_m/\partial\theta), \quad m = 0,1,2,\ldots, \quad (3)$$

where θ denotes temperature. Specifically, the PTM spectrum expected for the 3D-parabolic band transition in the bulk is given by

$$\hbar\omega S \propto (\hbar\omega - E_0) U(\hbar\omega - E_0), \quad (4)$$

while that for subband transitions in a quantum well is represented by

$$\hbar\omega S \propto \sum_n U(\hbar\omega - E_n). \quad (5)$$

This relation will be valid so far as the photothermally induced changes in the width and potential depth of the well are practically negligible so that $\partial E_n/\partial\theta$ is identical for every subband index n. Important implications of Eq. (5) are that the PTM spectrum $\hbar\omega S$ of the quantum well structure exhibits a staircase form with steps at photon energies $\hbar\omega = E_n$ and that the relative magnitude of the signal at each threshold energy E_n follows $E_n S(E_n)/E_1 S(E_1) = n$.

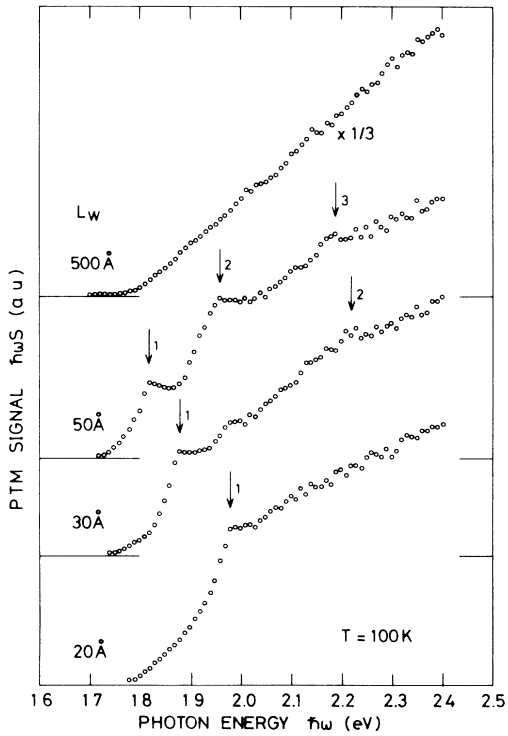

FIG. 1. PTM spectra $\hbar\omega S$ measured on a-Si–a-SiC multilayers with a-Si well-layer thicknesses $L_W = 20$, 30, 50, and 500 Å at temperature 100 K. The arrows indicate the energy positions of step edges.

Figure 1 presents the PTM spectra $\hbar\omega S$ measured on the multilayered structures with the a-Si:H well-layer thicknesses $L_W = 20$, 30, 50, and 500 Å, as functions of photon energy $\hbar\omega$. Interference fringes which usually perturb the PTM spectrum on the lower photon-energy side have been averaged out. For $L_W = 500$ Å, it is clearly found that the spectrum has a linear dependence on the photon energy. Similar spectra have been obtained for multilayered structures of $L_W \geqq 100$ Å, as well as in unlayered (bulk) a-Si:H films. This behavior is in good agreement with that predicted for the unquantized regime. We have confirmed that the threshold energy E_0 determined with Eq. (4) is completely equivalent to that determined by the Tauc plot, according to Eq. (1), over a temperature range from 100 to 300 K.

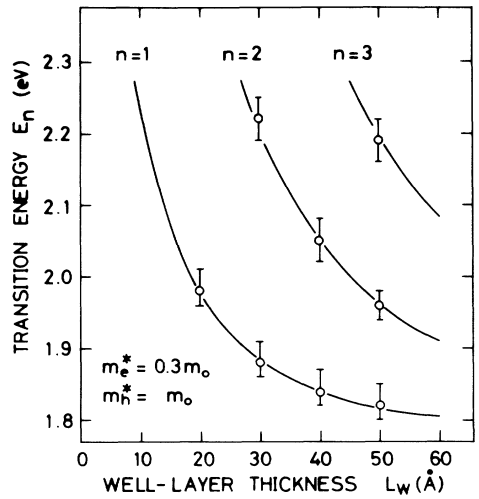

FIG. 2. Subband transition energies E_n ($n=1,2,3$) as functions of the well-layer thickness L_W. Circles are experimental data, and solid lines the theoretical plots calculated from the one-dimensional quantum well model.

The spectral shapes of the PTM signal for $L_W \leqq 50$ Å are entirely different from that for $L_W = 500$ Å. These spectra clearly exhibit the staircase behavior expected from Eq. (5). The energy positions of step edges are indicated by arrows in the figure. As found for the case of $L_W = 50$ Å, the energy interval between the step edges becomes longer at higher photon energy, indicating that the optical interference effect is excluded for the explanation. It may be, therefore, plausible to identify the staircase behavior as originating from subband transitions, so that the energy position of each step edge is related to the threshold energy E_n for the transition. If these assignments are correct, then the relative magnitude of the signal at each suggested threshold energy E_n should follow $E_n S(E_n)/E_1 S(E_1) = n$, as mentioned previously. This relation can be readily confirmed in the experimental data in Fig. 1, suggesting the plausibility of the present assignments for threshold energies. On the other hand, the deviation from an ideal staircase form, that is, the spectrum broadening, may be associated with microscopic fluctuations of the *a*-Si:H well-layer thickness as well as the contribution from transitions involving localized tail states which may still remain below the lowest subband edges. In addition, the effect of collisions may be included as a possible mechanism for the spectrum broadening.

In our recent work on in-plane carrier transport in *a*-Si:H–*a*-SiC:H multilayers by the transient grating method,[10] an anomalous increase in the carrier diffusion length was observed when the *a*-Si:H well-layer thickness L_W was decreased below 50 Å. The result led us to conclude that the carrier transport takes place at the subband states in the *a*-Si:H quantum well for $L_W \leqq 50$ Å. The present observation of subband transitions for $L_W \leqq 50$ Å is consistent with the conclusion reached by the transport experiment.

The threshold energies E_n for the transition between the nth subband states are summarized in Fig. 2 as a function of the well-layer thickness L_W. The threshold energies are easily calculated on the basis of the one-dimensional quantum well model. The results of the calculation, fitted to the experimental data, are plotted by solid lines. Here the electron (m_e^*) and hole (m_h^*) effective masses are chosen as $0.3m_0$ and m_0, respectively, in both sublayer regions, where m_0 denotes the free-electron mass. As found in the figure, the theoretical plots yield good fits to the experimental data. Identical values of effective masses are deduced from electroabsorption measurements on *a*-Si:H–*a*-SiC:H multilayered structures,[11] whereas a larger electron mass ($m_e^* = 0.6m_0$) is suggested by the analysis of the resonant-tunneling phenomenon in *a*-Si:H–*a*-Si_3N_4:H double-barrier structures.[12] This disagreement is likely to be reconciled if the difference in the electron mass of the well material and the barrier material is adequately taken into account in each experiment.

In summary, PTM spectra of the *a*-Si:H well layers have been investigated on *a*-Si:H–*a*-SiC:H multilayered structures. The spectra for the well-layer thickness less than 50 Å exhibit staircase form. The staircase behavior is interpreted as arising from the subband transitions in the *a*-Si:H quantum well. The experimental data for the transition energies are consistent with those expected from the one-dimensional quantum well model involving a selection rule for the transition between the confined states.

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