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MULTILAYERED AMORPHOUS SILICON STRUCTURES

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Ultra-thin multiple layered structures which consist of hydrogenated amorphous silicon (a-Si:H) and silicon nitride (a-Si1-xNₓ:H) have been systematically studied as a new class of semiconductor superlattices. The layer thickness can be controlled on an atomic scale, and hence the optical and electrical properties have been interpreted by assuming the quantized states in the potential well layers, as in the case of crystalline semiconductor superlattices. The existence of the quantized levels in the a-Si:H well layer has been directly demonstrated by observing the resonant tunneling current through a-Si:H/a-Si3N4:H double barrier structures. Novel thin film transistors (TFTs) in which the a-Si:H/a-Si1-xNₓ:H multilayer is employed as an active region have been designed and fabricated.

1. INTRODUCTION
Each of amorphous semiconductors composed of random network has its own short range order in terms that the nearest neighbour interatomic distance or bond length is basically identical to that of the corresponding crystalline phase. Artificially designed periodic potential structures produced by amorphous semiconductor multilayers are, therefore, regarded as an amorphous superlattice. In particular, ultra-thin multilayered structures consisting of hydrogenated amorphous silicon (a-Si:H) and silicon-based compounds such as a-Si1-xCx:H, a-Si1-xNₓ:H, a-Si1-xOₓ:H and a-Si1-xGex:H have been extensively studied[1-5]. In this paper, we describe recent studies on the structural, optical and electrical properties of a-Si:H/a-Si1-xNₓ:H multilayers and demonstrate the novelty of this material.

2. PREPARATION OF MULTILAYERED STRUCTURES
Ultra-thin a-Si:H and a-Si1-xNₓ:H layers were alternatively deposited by the glow discharge decomposition of an SiH₄ gas and an SiH₄+NH₃ gas mixture, respectively. The nitrogen content X in a-Si1-xNₓ:H was controlled by changing the gas molar fraction of [NH₃]/[SiH₄]. The preparation method of the multiple layered structures is described in detail in a previous work[4]. For the purpose of obtaining the abrupt interface and of preparing the uniform ultra-thin layers with desired chemical compositions, the deposition time for the individual layer growth was kept much longer than the residence time of the reactive gases in the reactor. In addition, the glow discharge was turned off at each step of the individual layer deposition, and the reaction chamber was pumped down to 10⁻³ Torr and purged with hydrogen gas.

3. STRUCTURE OF AMORPHOUS SUPERLATTICES
Evaluation of amorphous multilayers was performed by Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), x-ray diffraction and
transmission electron microscopy[1-3]. X-ray diffraction of the multilayers clearly shows the periodic nature associated with the well defined superstructure. Figure 1 represents a typical diffraction intensity curve plotted against scattering angle. The specimen was designed so as to contain 30 periods of 25 Å thick a-Si:H well layer and 100 Å a-Si3N4:H barrier. The x-ray diffraction measurements for the multilayers deposited on c-Si substrates were carried out by using CuKα (λ = 1.5418 Å) radiation. In the figure, the first Bragg peak is not observed since it must appear at a very low angle of about 0.7 degrees. The layer spacing is determined to be 124 Å from the positions of the Bragg peaks observed in Fig. 1. This value is in good agreement with the layer thickness (125 Å) estimated from the deposition rates of the individual layers. Also, the measured full width at half maximum (FWHM) in the 2θ scan is about 0.1 degrees, indicating that the deposited layers are smooth and parallel on an atomic scale and the a-Si:H/a-Si3N4:H interface is abrupt enough to reveal quantum size effect. Additional information on the layered structure is derived from x-ray rocking curves obtained by holding the specimen around the Bragg angle. Figure 2(a) shows a rocking curve for the 2nd Bragg peak observed in Fig. 1. A sharp peak of the FWHM ≈ 0.04 degrees strongly supports the existence of the well defined layered structure. However, there exists a weak satellite peak at about +0.06 degrees away from the main peak. This subpeak is clearly observed in the rocking curve optically aligned for the subpeak (Fig. 2(b)). This implies the presence of monolayer steps and/or local mosaic structures in the multilayers[2]. The monolayer steps possibly existing in the multilayers could be ascribed to the fact that Si-N-Si bond formation at the interfaces does not necessarily proceed through the same growth process for the case of a-Si:H deposition on a-Si3N4:H and for a-Si3N4:H on a-Si:H. Also, a surface smoothing mechanism arising from enhanced surface diffusion of adsorbed species might be involved in the plasma deposition process, resulting in surprisingly flat interfaces.

4. OPTICAL PROPERTIES
4.1 OPTICAL BANDGAP

For the well-defined, ultra-thin layered structures in which the potential well width is in the range of a carrier de Broglie wavelength and the inelastic carrier
Fig. 2 Rocking curves around the 2nd Bragg angle for the sample shown in Fig. 1 measured by aligning for the main peak (a) and the subpeak (b), respectively.

4.2 PHOTOLUMINESCENCE

Photoluminescence (PL) spectra for a-Si:H (8 ~ 400 A)/a-Si$_3$N$_4$:H (100 A) multilayers consist of an emission band arising only from a-Si:H well layers when the specimen is excited with 514.5 nm light from an Ar$^+$ ion laser. The spectrum for the multilayer having a well layer thickness of more than 100 A was basically similar to that for bulk a-Si:H while the spectrum for the thinner well width than 50 A was different from the bulk one. The blue shift of peak energy and broadening of FWHM were observed as the well layer thickness decreases below 50 A. Note that the luminescence occurs through radiative recombination of electrons and holes trapped by the band tail states[7]. The quantization in the extended states modifies
The optical bandgap $E_{\text{opt}}$ and the slope of the Tauc plot $\sqrt{\alpha}$, as a function of well layer thickness for a-Si:H/a-Si$_3$N$_4$:H(100 Å) superlattices. Solid line indicates the calculated $E_{\text{opt}}$ by assuming the electron effective mass $m_e=0.6m_0$ and the hole mass $m_h=1.0m_0$.

Figure 3 The luminescence quenching by electric field applied perpendicularly to the layered structures was studied, in order to reveal the existence of the well-defined a-Si:H quantum well to confine electrons in the a-Si:H/a-Si$_3$N$_4$:H multilayers. The absence of built-in electric field in the superlattices and the spatial extent of carrier wave functions in the well layer are also clarified by PL quenching experiments. Figure 5 shows the luminescence intensity in the a-Si:H/a-Si$_3$N$_4$:H multilayers as a function of applied electric field perpendicular to the layered structures. In the range of the well layer thickness from 400 to 100 Å, the luminescence quenching due to the applied field becomes more pronounced with decreasing the well layer thickness, indicating that photogenerated holes and electrons are spatially separated. For smaller well layer thicknesses less than 50 Å, the quenching effect becomes less pronounced. In particular for the well widths less than 25 Å, the quenching effect is hardly observed because the photocarriers in the quantized levels can no longer spatially separated even at an electric field strength of $10^6$ V/cm. Therefore, it is likely that the spatial extent of carrier wave function is larger than 25 Å. Note that the clear observation of PL quenching by external electric field is a direct consequence of the absence of built-in field induced by interface defects.
Fig. 4 Integrated PL intensity as a function of well layer thickness.

Fig. 5 Integrated PL intensity as a function of applied field for a-Si:H/Si$_3$N$_4$:H(100 A) multilayers.
5. RESONANT TUNNELING

In order to directly prove the existence of the quantization effect in the amorphous multilayers, the current transport across the a-Si:H/a-Si$_3$N$_4$:H double barriers was examined, because the resonant tunneling of electrons through the quantized states in the a-Si:H well will yield current bumps on the current-voltage characteristics. Figure 6 represents measured current-voltage characteristics of a double barrier system with a well width of 40 Å, together with the calculated electron transmission coefficient $T^*T$ in the double barrier. The calculation of electron transmission coefficient in the double barriers was carried out, based on the WKB approximation[8] for the band profile with the conduction band discontinuity of 1.7 eV determined by XPS[6]. We assumed that electrons in the symmetric double barrier system at zero bias have a thermal energy of $kT/2$ and that externally applied bias is divided among the a-Si$_3$N$_4$:H barrier layers and the phosphorus doped a-Si:H well layer by considering the respective film thickness and permittivity. No significant structure or current bump is observed at 288 K because of the thermal smearing effect, while at 77 K the current bumps are clearly observed at applied biases of about 0.2, 0.4 and 0.9 volts. The current density is less sensitive to temperature as expected for the tunneling transport. Note that the voltages corresponding to these current bumps are in excellent agreement with theoretically predicted biases at which the resonant tunneling takes place when the electron effective mass $m_e$ is chosen as 0.6$m_0$. It must be emphasized that the electron effective mass obtained from the resonant tunneling experiments is consistent with that determined from the optical bandgap data for a-Si:H/a-Si$_3$N$_4$:H multilayers as shown in Fig. 3. Unfortunately, sharp resonant tunneling can not be detected in the

![Graph showing measured current-voltage characteristics and calculated electron transmission coefficient.]

Fig. 6 Measured current-voltage characteristics of a double barrier with the well layer thickness $L_w=40$ Å. Metal contact is positively biased. Also, the calculated electron transmission coefficient through the double barrier $T^*T$ at 77 K is plotted against applied bias.
real double barrier system at applied voltages corresponding to \( V_{\text{app}} \approx 1 \), because a considerable reduction of the resonance peak height and a significant broadening of the resonance bands are caused by electron scattering by structural defects and microscopic fluctuations of the layer thicknesses. And more essentially, the potential fluctuations arising from the lack of long range order must remarkably smear the quantized energy levels. The experimental result definitely indicates that the conduction electrons in a-Si:H can be quantized even in the potential well with a layer thickness of 40 A, indicating that the free electron wave function in a-Si:H must extend over at least 40 A in consistence with the result of electric field quenching of luminescence.

6. APPLICATIONS

Based on better understanding of the quantum size effect in the multilayers, novel thin film devices such as superlattice TFTs, EL diodes and solar cells have been designed and fabricated [9-11]. The superlattice TFT is expected to have unique features as follows: (1) The electrons confined in an a-Si:H well layer exhibit quasi-two-dimensional natures and the mobility could be enhanced. (2) The surface band bending in the electron accumulation layer is moderated by the presence of a-Si\(_{1-x}\)N\(_x\):H barrier layers and hence the drop of field effect mobility due to the interface states could be reduced.

The superlattice TFTs with active layers consisting of a-Si:H/a-Si\(_{1-x}\)N\(_x\):H superlattices were fabricated in a reverse staggered electrode structure. Figure 7 shows the field effect mobility measured as a function of well layer thickness for the fixed a-Si\(_{1-x}\)N\(_x\):H barrier width of 50 A. The mobility remains almost unchanged (0.13 cm\(^2\)/Vsec) when the well layer thickness is reduced down to 50 A, below which it starts to increase and saturates around 0.70 cm\(^2\)/Vsec at well widths of less than 25 A. The well thickness at which the mobility starts to increase corresponds to the onset of the quantization in the a-Si:H conduction band as shown in Fig. 3. This appears to indicate that the quantized electrons less interact with the band tail states which deteriorate the mobility[9].

![Fig. 7 Electron field effect mobility as a function of well layer thickness for superlattice TFTs.](image-url)
7. CONCLUSIONS

It is demonstrated that a new class of semiconductor superlattices and quantum well structures are fabricated from the alternative deposition of a-Si:H and a-Si$_1$-X$_N$:H. It is found that the a-Si:H/a-Si$_1$-X$_N$:H interface is abrupt on an atomic scale and that there are no significant interface states which induce the built-in electric field in the system and deteriorate the luminescence efficiency from the a-Si:H well layer. For the well layer thickness below 50 Å, the existence of quantum size effects has been demonstrated from the blue shift of the optical absorption edge as well as of the luminescence peak energy and from the increase in the luminescence intensity. The photoluminescence quenching by electric field perpendicularly applied to a-Si:H/a-Si$_1$-X$_N$:H multilayers has indicated that the spatial extent of electron wave function in the a-Si:H well is larger than 25 Å. The direct evidence for the existence of the quantized levels in a-Si:H well layer has been obtained by observing the resonant tunneling current through a-Si:H/a-Si$_3$N$_2$:H double barriers. The superlattice TFTs have shown the enhancement of field effect mobility.

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