Artificially-Designed P-Type Amorphous Semiconductor Produced from Boron-Doped a-Si : H/ Undoped a-Si_{1-x}N_x:H Superlattices

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We have designed and synthesized a new class of doped superlattice consisting of B-doped hydrogenated amorphous silicon (a-Si:H) as a well layer and undoped a-Si_{1-x}N_x:H as a barrier. It is shown that this doped heterojunction superlattice can offer wide gap (≥ 1.75 eV), photoconductive ($\geq 10^{-6}$ Scm⁻¹) p-type materials.

1. Introduction

The optical and electronic properties of a-SiC:H/a-Si:H and a-Si1-xNx:H/a-Si:H multiple layered structures have recently been reported, $1^{1,4}$ and whether or nor the quantum size effect is observable in such superlattices has become one of key issues for understanding the physics of amorphous semiconductors. The superlattice structures consisting of a-Si:H well layers sequentially alternating with $a-Si_{1-x}N_x:H$ $(0.2 \leq x \leq 0.57)$ barrier layers have been prepared by the glow discharge technique. The a-Si:H/ $a-Si_{1-x}N_x$:H interface appears to be abrupt on an atomic scale,²⁾ and 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.³⁾ For the well layer thicknesses below 50 A, the existence of quantum size effects has been demonstrated from the blue shift of the optical absorption $edge^{1 \sqrt{3}}$ as well as of the luminescence peak energy and from the increase in the luminescence intensity.³⁾

In this paper, we report on wide gap, photoconductive p-type materials synthesized from the amorphous semiconductor superlattices in which boron-doped a-Si:H well layers are sandwiched with undoped $a-Si_{1-x}N_x$:H barrier layers.

2. Experimental

The B-doped $a-Si:H/a-Si_{1-x}N_x$:H multiple layers were deposited on quartz, Corning 7059

glass, and c-Si substrates by rf glow discharge technique. Boron-doped a-Si:H well layer was grown from a SiH₄ (10.3 % in H₂) + B_2H_6 (1.0 % in H₂) gas mixture. Successive deposition of undoped $a-Si_{1-x}N_x$:H was carried out in SiH₂ (10.3 % in H_2) + NH₃ (14.7 % in H_2) plasma. During the growth of each layer, substrate temperature, rf power and gas pressure were held at 300°C, 5 W and 0.2 Torr. respectively. In order to prepare the uniform ultra-thin layers with the desired chemical compositions and to obtain the abrupt heterojunction interfaces, the time of monolayer growth was controlled to be as long as possible (growth rate: 0.2 ~ 0.3 A/sec) compared to the residence time of the reactive gas in the reactor (~ 3 sec). The glow discharge was turned off and the reactor was purged with hydrogen gas at each step of the individual layer deposition. The boron doping ratio in a-Si:H and the nitrogen content x in a-Si1-xNx:H were controlled by changing the gas ratios of $[B_2H_6/SiH_L]$ and $[NH_3/SiH_L]$, respectively. The doped superlattices with 30 periods were prepared. The conductivity and its activation energy were measured by using co-planar Ni-Cr electrode evaporated in the gap cell structure on top of the superlattices. Photoconductivity was measured under AM1 light illumination (100 mW/cm^2).

3. Design of Superlattices

The periodric potentials in a-Si:H/ a-Si_{1-x} \mathbb{N}_x :H superlattices can be roughly

estimated if the electron affinities for the both materials are known. Since the electron affinities of B-doped a-Si:H and a-Si1-xNx:H used in the present experiment have not been measured, we assumed that the affinity of B-doped a-Si:H is the same value as measured for undoped a-Si:H (3.93 eV),⁵⁾ while the affinity of a-Si_{1-v}N_v:H (x=0.38) is estimated from the measured values of pure a-Si:H, a-Si_{0.8}N_{0.2}:H (3.90 ± 0.10 eV),⁴⁾ and stoichiometric $a-Si_{0.43}N_{0.57}$:H (2.20 eV)⁶⁾ by the interpolation using a quadratic equation. The energy band diagram for a B-doped a-Si:H/undoped a-Si0.62N0.38:H superlattice is illustrated in Fig. 1, where the measured optical gaps of 1.4 eV for bulk a-Si:H doped with more than 1 % boron atoms and 2.2 eV for bulk a-Si0.62N0.38:H are used.

For synthesizing wide gap, photoconductive p-type materials, the thicknesses of B-doped a-Si:H well layers and undoped a-Si_{1-x}N_x:H barrier layers must be optimized: The effective bandgap of the multilayer can be controlled by the well layer thickness, which determines the quantized levels of extended state carriers, and by the extent of the mutual coupling of the carrier wave functions which penetrate into the barrier layer. Based on the calculated quantized levels of carriers in a-Si:H well and the analysis of the wave function penetration into the a-Si_{1-x}N_x:H barrier, we adopted a well layer thickness less than 30 A and a barrier layer thickness of 17 A.

4. Results and Discussion

The optical gap E_{opt}, photoconductivity, dark conductivity and its activation energy of the synthesized superlattices composed of boron-doped a-Si:H well layer (25 A thick) and a-Si_{1-x}N_x:H (x=0.23 and 0.38) barrier (17 A thick) are shown in Fig. 2 as a function of boron doping ratio $[B_2H_6]/[SiH_4]$. In the figure, the photoconductivity and dark conductivity have the maximum values at a doping ratio of about 5 %. For the doped a-Si:H/a-Si0.77N0.23:H system, Eopt changes from 1.5 to 1.4 eV by increasing the boron doping ratio in the well layer and there is no clear indication of the existence of the quantum size effect (Fig. 2 (a)), while for the a-Si:H/ a-Si_{0.62}N_{0.38}:H system, E_{opt} decreases from 2.1 to 1.75 eV with increasing the boron doping ratio (Fig. 2 (b)). The value of E_{opt} for boron-doped bulk a-Si:H remains unchanged at 1.4 eV in the doping range 1 to 10 %. The photoconductivity of the doped superlattice exceeds 10⁻⁶ Scm⁻¹ over the boron doping range 2.5 to 10 %, where the conductivity activation energy decreases from 0.56 to 0.45 eV. Considering that the highly doped a-Si:H well layers are sandwiched by undoped a-Si_{0.62}N_{0.38}:H barrier layers with an optical gap



Fig. 1 The energy band diagram for a B-doped a-Si:H/undoped a-Si0.62N0.38:H superlattice.



Fig. 2 The optical gap, photoconductivity, dark conductivity and its activation energy of doped a-Si:H (25 A thick)/a-Si_0.77N_0.23:H (17 A thick) (a) and doped a-Si:H (25 A thick)/a-Si_0.62N_0.38:H (17 A thick) (b) multilayers as a function of boron doping ratio.

of 2.2 eV, conductivity of $\sim 10^{-10}$ Scm⁻¹, and its activation energy of 0.95 eV, and that a little autodoping of boron into a-Si1-xNx:H barrier layer, if exists, causes a decrease of the conductivity in the a-Si $_{1-x}\mathbb{N}_{x}$:H barrier layer, $^{7)}$ the measured net conductivity of the doped superlattice is expected to be significantly low. Nevertheless, the dark conductivity of 2.1x10⁻⁶ Scm⁻¹ and photoconductivity (AM1, 100 mW/cm²) of 6.5×10^{-6} Scm⁻¹ are obtained in the superlattice with 5 % boron-doped a-Si:H well layers, indicating that the carrier wave function in the extended states of the a-Si:H well layer sufficiently penetrates into the a-Si1_vNv:H barrier layer in agreement with the spatial distributions of the calculated carrier wave functions. The optical absorption tail below E_{opt} for the doped superlattice is significantly narrow (Fig. 3) and the slope of the Tauc plot associated with the steepness of the band edge is obtained to be $630 (eVcm)^{-1/2}$ for the 5 % B-doped a-Si:H $(25 \text{ A})/a-\text{Si}_{0.62}N_{0.38}$:H (17 A) superlattice, while $500 (eVcm)^{-1/2}$ for the 5 % B-doped bulk film. This difference in the optical absorption spectra is quantitatively explained by taking into account the quantization effect in the extended states.³⁾

For optimizing the well layer thickness, E_{opt} , photoconductivity, dark conductivity and its activation energy of the doped superlattices consisting of 30 periods of B-doped a-Si:H and $a-Si_{0.62}N_{0.38}$:H (17 A thick) were measured as a function of the well layer thickness. Photoconductivity and dark conductivity of the doped superlattices take their maximum values at a well layer thickness of about 25 A (Fig. 4). For the well layer thickness below 25 A, the decrease of the conductivity occurs primarily due to a decrease of the total number of boron atoms incorporated in the system because the barrier thickness and the layer number of superlattice are



Fig. 3 The optical absorption spectra of 5 % B-doped a-Si:H (25 A thick)/a-Si_{0.62}N_{0.38}:H (17 A thick) superlattice (SL) and 5 % B-doped a-Si:H bulk film (BULK).



Fig. 4 The optical bandgap, photoconductivity, dark conductivity and its activation energy of 5 % B-doped a-Si:H/a-Si0.62N0.38:H (17 A thick) superlattices as a function of the well layer thickness.

held constant. Further decrease of the well layer thickness below 15 A causes a decrease of the conductivity. This arises mainly from the quantum size effect which leads to an increase of the optical gap and conductivity activation energy.

Since the increase of nitrogen content in the barrier layer brings about the increase of $E_{\rm opt}$ due to the quantum size effect and the decrease of the barrier layer thickness gives rise to the increase of conductivity due to the tunneling effect of carriers in the well layer, it would be possible to synthesize photoconductive p-type materials whose $E_{\rm opt}$ and photoconductivity is as high as 1.9 eV and 10^{-5} Scm⁻¹, respectively, by controlling adequately the nitrogen content as well as the thickness of a-Si_{1-x}N_x:H barrier layer.

5. Conclusion

It is demonstrated that a new class of wide gap ($\geq 1.75 \text{ eV}$), photoconductive ($\geq 10^{-6} \text{ Scm}^{-1}$) p-type materials is synthesized by using the boron-doped amorphous superlattice structures, in which boron is doped only in the a-Si:H layers. Further optimization of doping level in the a-Si:H layer and of nitrogen content as well as the thickness of the barrier layer is in progress to synthesize p-type material with E_{opt} exceeding 1.9 eV.

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