Electrical and Optical Properties on Nanocrystalline Si/SiO₂ Superlattice for Solar Cell Emitters

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Abstract
In this study, we made the heterojunction solar cells on Si substrate by fabricating a nanocrystalline Si/SiO₂ superlattice emitter structure. Amorphous silicon and silicon dioxide superlattice were prepared by rf Si sputtering and plasma oxidation, respectively. The deposited amorphous silicon was crystallized at high temperature. Microstructure studies by TEM show that amorphous silicon was changed to nanocrystalline silicon. The optical bandgap of the superlattice depends on the Si layer thickness. Cells with an Al/ZnO:Al/(Si/SiO₂)n/Si structure show 1.4% conversion efficiency (Voc: 112mV, Jsc: 32.3mA/cm²). Furthermore, the optical and electrical properties of (Si/SiO₂)n/Si superlattice structure are reported.

1. INTRODUCTION

Silicon based nanostructures such as an ultra-thin silicon layer sandwiched between two SiO₂ films and an ultra-thin a-Si:H are a promising surface passivation approach and solar cell application formed by heterojunction. Ultra-thin silicon layer enclosed by SiO₂ films have already been reported for III-V compound semiconductors (Yablonovitch et al., 1985; Gruenbaum et al., 1991). Especially promising Si based nanostructures are SIPOS-type Si (SIPOS = semi-insulating polycrystalline Si) (Matsushita et al., 1979; Yablonovitch et al., 1985; Gruenbaum et al., 1991) or polycrystalline Si OPO (OPO = oxide/poly-Si/oxide) stacks (Gruenbaum et al., 1991) as a materials of wide energy band gap. Those structures are modeled as an one-dimensional superlattice device (Fischetti et al., 1985) as shown in figure 1. The SIPOS comprise the 44at% oxygen, 0.6at% phosphorus, and 55.4% silicon. The SIPOS structure experimentally showed an extremely low saturation current of 10⁻¹⁴ A/cm² and an excellent open-circuit voltage of 720 mV and surface recombination velocities of 200 cm/s in double heterojunction structures (Yablonovitch et al., 1985; Gruenbaum et al., 1991). Surface recombination for OPO stacks showed surface recombination velocity of 10~20 cm/s (Matsushita et al., 1979; Muramatsu et al., 1997). Ultra-thin amorphous silicon (a-Si:H) also shows good surface passivation property on crystalline silicon (c-Si) (Sawada et al., 1994). Heterojunction solar cell with a-Si/c-Si, for example HIT(heterojunction with intrinsic thin-layer) solar cell, shows around 20% conversion efficiency on 100mm² substrate (Taguchi et al.,2000)

In the present work, heterojunction structure with SiO₂/Si superlattice deposited on p-type Si silicon substrate was studied. A surface passivation scheme on low resistivity n-type Si wafer was also investigated to find out the optimal Si deposition condition. The thin thermal oxide with 2nm thick and thin Si with various thicknesses was used to determine the surface passivation velocity, measured by a contactless photoconductance decay method (Kane et al., 1985). The optical properties of sputtered Si and plasma oxidation were investigated by UV-VIS reflection measurement and optical simulation program. With optimal deposition conditions, we fabricated a heterojunction solar cell with a (SiO₂/Si/SiO₂) superlattice on p-type Si substrate. I-V characteristics was measured by a quasi-steady-state open circuit voltage method (Sinton et al., 2000).
2. FABRICATION OF SiO$_2$/Si/SiO$_2$ HETEROJUNCTION STRUCTURE

2.1 Si/SiO$_2$ SUPERLATTICE

The amorphous silicon deposition by RF magnetron sputtering was firstly considered to find out optimal deposition condition. The sputtering condition was as follows: After a base pressure of $1\times10^{-4}$ Pa was reached, the argon flow was turned on and the silicon target (0.002 ~ 0.008 $\Omega$cm, phosphorus doped n-type) was pre-sputtered for 10 minutes. Then, a thin (13-550 Å) a-Si film was deposited on the substrate at a rate of ~0.26 Å/s and at a pressure of 1.5 Pa. The RF power during the a-Si deposition was set to 30W to reduce plasma damage. For SiO$_x$ deposition, in addition to Ar gas, the chamber had a constant inflow of oxygen (~13sccm). Oxygen caused plasma oxidization of Si atoms on their way to the substrate and that resulted in deposition of SiO$_x$. The sputtering parameter for SiO$_x$ deposition was 2Pa for the pressure, 20W for RF power and resulting deposition rate is ~0.016nm/s. The sputtering conditions for silicon were characterized by surface passivation velocity (Cho et al, 2002). The SiO$_2$/Si/SiO$_2$ quantum well structure was deposited on the high resistivity n-type silicon wafer, where rear surface oxidize with thick oxide (~100nm). Then surface recombination velocity was measured by photoconductance decay method (Kane et al., 1985). The result from single quantum well (QW) and double QW is shown in Fig. 2. The surface recombination velocity for thin well (~13Å) is same as that of thick (~100nm) thermal oxide.
2.2 HIGH TEMPERATURE ANNEALING

Compared to lattice matched nanostructure, for example GaAs based multiple quantum wells, silicon nanostructure is much more difficult to produce clean junction with higher bandgap materials. Opposite approach was proposed by Abeles and Tiedje (1983). Because lattice constant in amorphous semiconductors, for example SiC, SiNₓ, and SiO₂, no longer exists, the requirement concerning lattice mismatch in silicon superlattice can be relaxed by amorphous structure. In this paper, we used SiO₂ as a higher bandgap material in superlattice structure. However, the quality of Si (i.e., amorphous silicon) by deposited on the amorphous substrate (SiNₓ and SiO₂) is poorer than their crystalline counterparts, so that electron mean free path in a-Si/amorphous SiNₓ and SiO₂ superlattice is reduced by poor interface (i.e., roughed interface). Further high temperature annealing is required to crystallize thin a-Si layer in Si/SiO₂ superlattice (Zacharias et al., 2000) and improve interface quality (Jelenkovic et al., 1997). Note that the temperature required for the crystallization of the ultra-thin a-Si films sandwiched between two SiO₂ layers is much higher than the normal crystallization temperature of 500-700°C for ‘thick’ (> 50 nm) a-Si films (Zacharias et al., 2000). At a high temperature, either SiO₂/Si intermixing caused by oxide breakdown reported Miranda et al (1998) and layer separation of Si and SiO₂ (Zacharias et al., 2000) possibly happen. Fig. 3 shows the transmission electron microscope (TEM) result of 5 bilayers of Si and SiO₂ after 950°C and 1100°C furnace annealing. Density difference in Si and SiO₂ layers make white and dark image in TEM image. From the Raman spectra as shown in Fig. 4, the crystallization of the a-Si layer start from 950°C and the annealing behavior above 1000°C is almost same. However we could not able to take silicon lattice image from those samples so that the annealed Si superlattices at temperature of 1000°C~1100°C for 30 minutes still have the short range order, i.e., grain size is very small (<1nm), and partially crystallize with less than 1nm grain size. The Si layer with small grain is not fulfilled the above mention requirement. However, we fabricated nanocrystalline Si(nc-Si)/SiO₂ superlattice with improved Si deposition condition, reported in this conference (Xia et al., 2002). The basic difference between nc-Si/SiO₂ and superlattice in Fig. 3 originates from density of Si layer, i.e., void ratio in Si films. The deposited suboxide SiOₓ also separate as Si and SiO₂ by high temperature annealing without layer intermixing shown in Fig. 3. We think oxide layer become SiO₂ after layer separation by annealing.

Figure 3. TEM image of Si/SiO₂ multilayer with ~35 Å Si and ~40 Å SiO₂ thicknesses on quartz substrate. (a) 950°C annealing and (b) 1100°C annealing.

Figure 4. Raman spectra of Si/SiO₂ bilayers with ~40 Å Si thickness. The annealing was done by normal furnace in N₂ atmosphere for 30 minutes.
2.2 HETEROJUNCTION SOLAR CELLS

To study the superlattice as an emitter, we deposited 20 Å Si and 30 Å SiO₂ on one side polished, boron doped (1~2Ωcm) p-type silicon substrate. The Si substrate was cleaned by RCA cleaning and removed native oxide in dilute HF solution. The silicon substrate immediately loaded into sputtering chamber to deposited SiOₓ and Si up to 20 bilayers on polished Si surface. The Si/SiO₂ superlattice annealed at 1000°C degree for 30 minutes to crystallize the Si layer. ZnO:Al (ZnO doped with Al) by RF-sputtering was used for transparent conductive oxide (TCO) to make good contact between Si/SiO₂ superlattice and top metal contact. The conductivity of the fabricated ZnO:Al films, measured at the central spot of the substrate, is the function of RF power, film thickness, and substrate temperature. To obtain higher conductivity, RF power of 120W and substrate temperature of 200°C was used to deposit 0.35mm thick ZnO:Al thin film (Song et al., 2002). Finally Al was evaporated on the top and bottom surface.

Figure 5. (a) schematic structure for Si/SiO₂ superlattice heterojunction solar cells and (b) HRTEM image of Si/SiO₂ superlattice with 20 bilayers.

3. OPTICAL PROPERTIES OF THIN Si AND SiOₓ

Reflection spectra were taken over the range 300-1000 nm at 8° incidence angle with a double beam UV/VIS Cary 5 spectrophotometer. The beam size on the sample was approximately 3 x 5 mm. Spectra were corrected by comparison to a reference of the polished silicon. Measured spectrum was fitted with approximate structure model using optical simulation program, WVASE 32 from J.A. Woollam Co, Lincoln, 1998. For the optical constants to be determined, the thickness of each layer was adjusted until a good fit was obtained between the calculated performance and the experimental spectrum. Fig. 6 shows the optical constant of deposited Si and SiOₓ layers. The refractive index in given as-deposit a-Si is lower than that of crystalline silicon, which means that the void ratio for three different thicknesses by effective mass approximation of a-Si and void is around ~50%. The refractive index for 1.9nm Si is higher than that of 6.2nm and 12.6nm Si indicate that Si with 1.9nm thick has more dense than thicker Si, which is opposite trend reported by Khriachtchev et al. (2001). We assume the Si quality is different, whereas the refractive index of Si deposited at lower pressure has the same trend as reported by Khriachtchev et al. (2001).

Figure 6. Optical constant of (a) sputtered silicon and (b) SiOₓ.
The optical bandgap $E_g$ can be determined from optical absorption $\alpha \cdot h \nu$ data, where $\alpha$ is absorption coefficient of the material and $h \nu$ is the energy of the photon, by extrapolating the linear relation portion of high energy in the plot of $(\alpha \cdot h \nu)^{1/2}$ versus $h \nu$ to zero ordinate, i.e., the Tauc rule (Novikov et al., 1997).

Using this method, the optical bandgap $E_g$ for superlattice, Si thickness is 1.9nm, is found to be 2.30eV. However, the optical bandgap of the superlattice with thick Si layer ($>4$nm) is almost same as that of silicon as shown in Fig. 7.

4. ELECTRICAL PROPERTIES OF Si/SiO$_2$ SUPERLATTICE HETEROJUNCTION

Cells with an Al/ZnO/(Si/SiO$_2$)$_n$/Si substrate structure shown in Fig. 5 measured by a quasi-steady-state open-circuit voltage method (Sinton et al., 2000). The cell area is 4.8cm$^2$ (3.2cm $\times$ 1.5cm). 1.4% conversion efficiency with Voc of 112mV, Jsc of 32.3 mA/cm$^2$, and fill factor of 35% was achieved. Voc is much lower than that of double heterojunction SIPOS structure, i.e., measured Voc was 720mV (Yablonovitch et al., 1985). The problem with lower Voc would be either plasma damage during the Si/SiO$_x$ deposition or energy band mismatch in Si/SiO$_2$ superlattice and Si substrate. The material deposition by plasma generally creates the “plasma damage” in a semiconductor bulk and surface. This damage could be charge build-up, defect creation, or impurity contamination. If the sample suffers plasma damage and cannot be recovered, the damage should act as a recombination centre and reduce Voc. The basic difference between surface passivation scheme in Fig. 2 and Si/SiO$_2$ superlattice in Fig. 5(b) is the first thin oxide. In Fig.2, we used low temperature thermal oxide ($\sim$520°C) to grow 2nm thick SiO$_2$. In other hand, all oxide layer in Fig. 5(b) is sputtered SiO$_x$ with extremely low deposition power (30W). Lower RF power has the merit to control the layer thickness and possible reduce the defect generation by lower energy radicals. The plasma damage can be recovered by H$_2$ annealing in furnace (Muramatsu et al., 1997) and it is hard to find out the defects in TEM in Fig. 5(b). However, when we replace first oxide as thin thermal oxide around ~2nm, higher performance can be expected. The bandgap mismatch is still questionable. We only used one Si target to fabricate Si/SiO$_2$ superlattice emitter on p-type Si and n-type (100) substrate with 1~2 $\Omega \cdot $ cm resistivity. Further spatial studies with the different Si substrates and deposition targets are required. One promising result in this conference shows that fully crystallized nc-Si/SiO$_2$ can fabricate by optimal Si deposition (Xia et al., 2002).
5. CONCLUSIONS

The nc-Si/SiO₂ superlattices with small grain size fabricated by RF magnetron sputtering and following high temperature annealing. The optical bandgap of Si/SiO₂ superlattice with 1.9nm Si thick is found to be 2.3eV, whereas the superlattice with thicker Si is almost as that of bulk Si. The key factor to crystallize thin Si layer is depending on Si deposition condition, i.e. density of Si layer. Cells with Al/ZnO:Al/(Si/SiO₂)₂₀/Si structure (Subscript ‘20’ means the number of pair Si/SiO₂) shows higher Jsc (32.3mA/cm²), but the Voc need to improve up to 720mV from double heterojunction (heterojunction on front and rear) structure. Plasma damage seems be relaxed by lower RF power and high temperature annealing. However, further study is required to solve out bandgap mismatch in Si/SiO₂ superlattice and Si substrate. One promising result shows that fully crystallized nc-Si/SiO₂ can fabricate by optimal Si deposition.

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7. REFERENCES


