Hydrogenated microcrystalline silicon films prepared by VHF-PECVD and single junction solar cell

ZHIMENG WU*, QINGSONG LEI, JIANPING XI
Research Institute of Micro/Nano Science and Technology, Shanghai Jiao Tong University, Shanghai 200030, People's Republic of China
E-mail: Zhimengwu@hotmail.com

YING ZHAO, XINHUA GENG
Institute of Optoelectronics, Nankai University, Tianjin 300071, People's Republic of China

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Intrinsic microcrystalline silicon films have been prepared with very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD) from silane/hydrogen mixture at 180°C. The effect of silane concentration and discharge power on the growth of silicon films was investigated. Samples were investigated by Fourier transform infrared spectroscopy, Raman scattering and X-ray diffraction. The Raman spectrum shows that the morphological transition from microcrystalline to amorphous occurs under conditions of high silane concentration and low discharge power. X-ray diffraction spectra indicate a preferential growth direction of all microcrystalline silicon films in the (111) plane. In addition, a solar cell with an efficiency of 5.1% has been obtained with the intrinsic microcrystalline layer prepared at 10 W.
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1. Introduction

As a promising material for opto-electronic devices such as solar cells and thin film transistors, microcrystalline silicon has attracted many researchers to study it [1–3]. The conventional technique for growing microcrystalline films is the radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD) [4]. The typical growth rate in RF-PECVD is approximately 1 Å /s. However, microcrystalline solar cells require a thick active layer (about 1.5 μm) for its low optical absorption. The very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD) is beneficial for microcrystalline silicon growth and can provide high growth rate of microcrystalline silicon for commercial production [5–7].

In this paper, VHF-PECVD has been applied to deposit intrinsic silicon films at low temperature. We investigated the effect of silane concentration and discharge power on the growth of films. Electrical properties, hydrogen content and structural properties were presented. Finally, a solar cell was prepared to show the material result.

2. Experimental details

Two series of intrinsic silicon films were prepared on glass substrate by a capacitive-coupled PECVD system at a excitation frequency of 60 MHz. Electrode distance from the cathode to anode was 20 mm. Silane diluted in hydrogen was fed as the source gas and we kept the total flow gas constant at 60 sccm. The pressure of the source gas was kept at 0.9 Torr. The substrate temperature was 180°C. The silane concentration (SC = $SiH_4/(SiH_4 + H_2)$ was varied from 2 to 8% at the power of 20 W while keeping other parameters fixed. The discharge power was varied from 10 to 45 W while keeping other parameters fixed.

The dark conductivity was measured with an aluminous coplanar contact at room temperature using Keithley 617. The hydrogen content was calculated from Fourier transform infrared spectroscopy (FTIR) [8]. Raman spectrum and X-ray diffraction were used to characterize the crystallinity of the silicon films. The Raman scattering experiment was performed using 632.8 nm He-Ne laser. X-ray diffraction was performed using Cu-Kα radiation source in the range of 25 to 60°.

*Author to whom all correspondence should be addressed.

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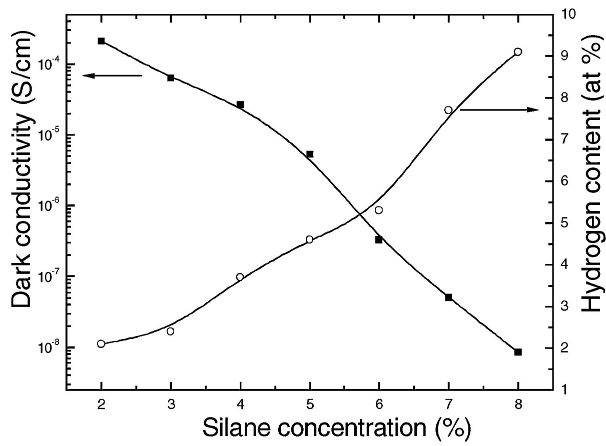

Figure 1 Dark conductivity and Hydrogen content for films deposited at different silane concentration.

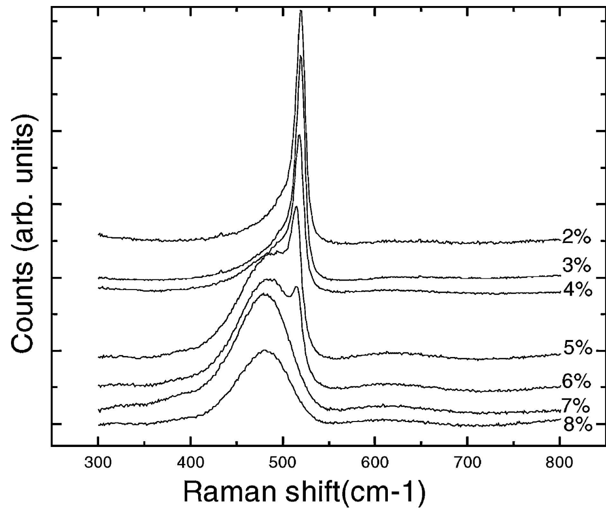

Figure 2 Raman spectra for films deposited at different silane concentration.

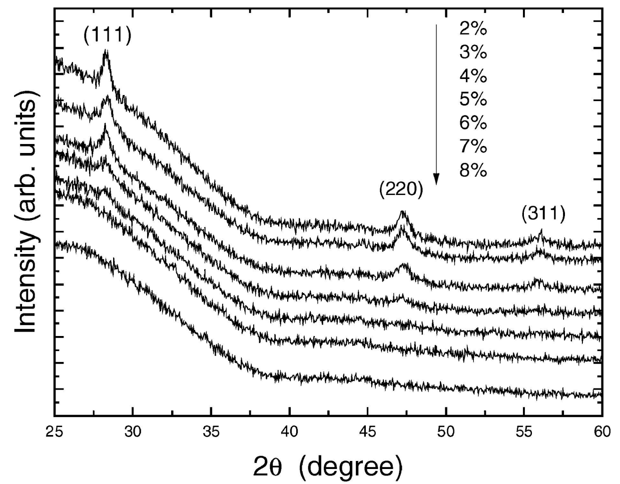

Figure 3 X-ray diffraction data for films deposited at different silane concentration.

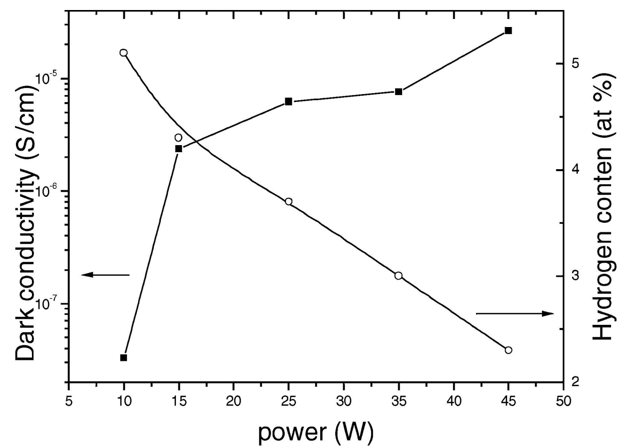

Figure 4 Dark conductivity and Hydrogen content for films deposited at different power.

3. Result

In the first part, intrinsic films prepared at different silane concentrations have been studied. Fig. 1 shows the dark conductivity and hydrogen bonded content as a function of silane concentrations. The dark conductivity decreases with the increase of silane concentrations. At SC of 2%, the dark conductivity is 2.1×10^{-4} S/cm. Increasing the silane concentration to 8% leads to a decrease of dark conductivity to 8.56×10^{-9} S/cm. In contrast, towards large silane concentration the hydrogen bonded content calculated form FTIR is enhanced from 2 at% to 9 at%.

The Raman spectra of silicon films deposited at different silane concentrations were compared in Fig. 2. The transition from microcrystalline silicon to amorphous silicon can be observed from the spectra. The intensity of the transverse optic (TO) peak of c-Si at 520 cm^{-1} is reduced with the increase of silane concentrations and disappears when the silane concentration exceeds 6%. The peak near 480 cm^{-1} appears at SC of 5% and is dominant at higher SC. The transition from microcrystalline to amorphous phase occurs at SC of between 5 and 7%.

The change in the structural composition is proved by XRD analysis. Fig. 3 shows the XRD spectra of silicon films deposited at different silane concentration. Three peaks corresponding to (111), (220) and (311) planes can be observed with a preferential orientation of (111) which is different with Ref. [9]. The diffraction peaks decrease with the increase of silane concentrations. At SC of 6%, the peaks of (220) and (311) are hard to be observed. The silicon films have no diffraction peaks at SC above 7%, namely the films are purely amorphous.

In the second part of this work, films have been prepared with SC of 4% at different power. Fig. 4 shows the dark conductivity and hydrogen concentration as a function of discharge power. The dark conductivity is enhanced from 3.3×10^{-8} S/cm to 2.64×10^{-5} S/cm when the power is increased. This increase in dark conductivity is accompanied by a decrease in the hydrogen concentration. The hydrogen content is reduced from 5.1 to 2.3 at%.

The intensity near 520 cm^{-1} is enhanced with the increase of discharge power (Fig. 5). Though the dark conductivity of films prepared at 10 W is 3.30×10^{-8} S/cm,

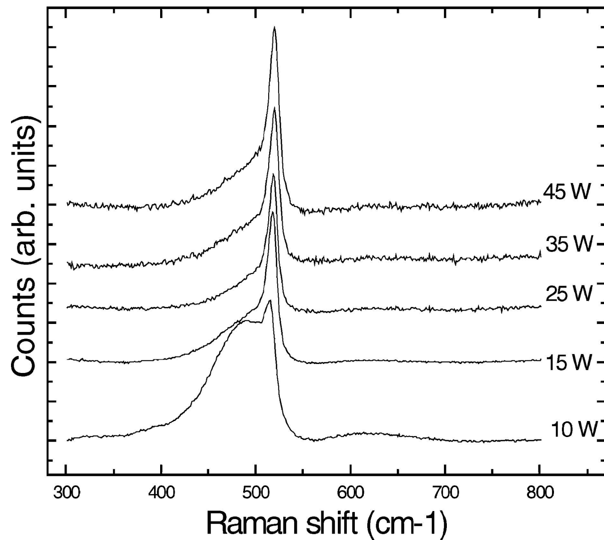

Figure 5 Raman spectra for films deposited at different discharge power.

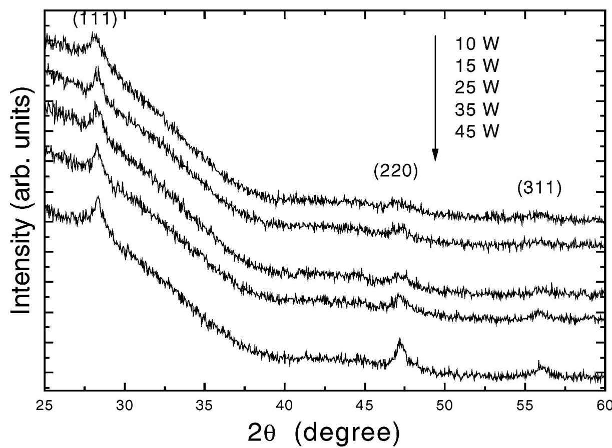

Figure 6 X-ray diffraction data for films deposited at different discharge power.

we still observed a peak near 520 cm^{-1}. At the power of 10 W, the intensity near 480 cm^{-1} is dominant while the peak near 520 cm^{-1} is small. Increasing the power leads to the increase of the intensity near 520 cm^{-1}. The XRD spectra of silicon films deposited at different power is compared in Fig. 6. The increase of discharge power leads to an increase of three peaks corresponding to (111), (220) and (311), thus the crystallite size in the (111) direction, evaluated applying the Debye-Scherrer formula, is enhanced at larger discharge power.

4. Discussion

This study confirms the effect of different SC and discharge power on the growth of silicon films. Intrinsic microcrystalline silicon films can be deposited using low SC and high discharge power. The atomic hydrogen-etching model can be applied to explain the change of crystallinity [10, 11]. At low SC and high discharge power, the silane is depleted by the reaction between silane and atomic hydrogen. The atomic hydrogen breaks weak Si—Si bonds involved in the amorphous structure and new strong Si—Si bonds (crystalline structure) is produced through the etching. Continued increasing SC or decreasing discharge power, the silane reacts with atomic hydrogen and the atomic hydrogen density is too low to change the structure of films, under this condition the growth of amorphous silicon is favorable. The morphological transition influences the hydrogen content and dark conductivity. In microcrystalline silicon films, the hydrogen is bonded at the surface of microcrystalline grains and in the amorphous phase [8]. When increasing silane concentration and decreasing discharge power, the enhancement of the amorphous volume fraction leads to the increase in hydrogen content and the decrease of the dark conductivity for the low conductivity of amorphous silicon.

It should be noted that high power increases the ion bombardment on the growing surface and produces high defect density which deteriorates the performance of solar cells [12, 13]. So for applied in microcrystalline silicon solar cells the films near morphological transition and prepared at low power is preferred [14]. The films deposited at 10 W in this work have a photosensitivity of from 500 to 3000, thus it can be used as the active layer in thin film solar cells. We have successfully prepared a microcrystalline silicon *pin* single junction solar cell with an efficiency of 5.1%. The intrinsic layer thickness is 1 μm. Fig. 7 shows the cell's J-V curve under AM1.5, 100 mW/cm^2, room temperature.

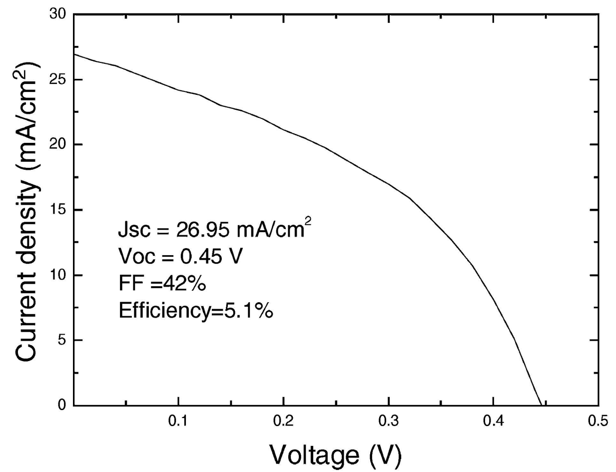

Figure 7 J–V curve of microcrystalline silicon *pin* single junction solar cell.

5. Conclusions

Device grade microcrystalline silicon films have been deposited on the glass substrate by varying SC and discharge power. The morphological transition is observed with changing SC and discharge power. At low SC and high power, the silicon films are microcrystalline and the preferred growth direction is (111). Accompanied by a decrease of dark conductivity and a increase of the hydrogen

content, the structure of silicon films shift from microcrystalline to amorphous when increasing SC or decreasing discharge power. The intrinsic microcrystalline silicon was applied to a solar cell as the absorber layer and a cell with an efficiency of 5.1% was obtained.

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