Solid State Science and Technology, Vol. 15, No 2 (2007) 92-97
ISSN 0128-7389

DEPOSITION OF HYDROGENATED NANOCRYSTALLINE SILICON (nc-Si:H) FILMS BY PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION

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ABSTRACT

In this work, hydrogenated nanocrystalline silicon (nc-Si:H) thin films were deposited by radio-frequency Plasma Enhanced Chemical Vapour Deposition (rf-PECVD) technique on crystal silicon (c-Si) substrate at different rf power with a constant silane to hydrogen partial pressure ratio. The effects of rf power on the structural properties of nc-Si:H films deposited on c-Si substrate were studied using Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), micro-Raman spectroscopy, and scanning electron microscopy (SEM). The RF power showed influence on the structural properties of nc-Si:H films. The presence of nanocrystallite clusters in the film structures was observed strongly at low rf power.

INTRODUCTION

Hydrogenated nanocrystalline silicon (nc-Si:H) has received a great deal of attention in the last decade in electronic device applications due to their improved transport property, higher electron mobility and lower degradation in light as compared to their amorphous counterparts [1]. The nc-Si:H thin films are known to consist of a two-phase-mixed material of silicon nanocrystalllites embedded within an amorphous silicon matrix [2]. Studies have shown that quantum size effects of the silicon nanocrystallites contribute to the unique and useful features of this material [3]. This natural quantum confinement system is composed of approximately 50% nanometre crystallite size silicon grains with grain size of 3 to 5 nm embedded within 50% of amorphous Si of 2 to 3 atomic spacing thick [4]. The nc-Si:H film is formed when silane (SiH_4) is highly diluted in hydrogen (H_2) gas in plasma enhanced chemical vapour deposition (PECVD) process. During this deposition process, H atoms enhance the atom mobility, reduce dangling bond defects, etch off disordered phases, modify the Si-Si network and reconfigure the subsurface bonds [5] forming the nanocrystalline structure within the amorphous phase.

In this work, a series of nc-Si:H films were deposited on crystal silicon (c-Si) substrates using a home-built radio frequency plasma enhanced chemical vapour deposition (rf-PECVD) system to investigate the effects of rf power on the structural and chemical bonding properties of nc-Si:H thin films. The structural properties of these films were investigated using x-ray diffraction (XRD) technique and micro-

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Raman spectroscopy while the Fourier transform infrared (FTIR) spectroscopy was used to study the chemical bonding properties of the films.

EXPERIMENTAL DETAILS

Hydrogenated nanocrystalline silicon films were deposited on Si (100) substrates at 200°C using a home-built rf-PECVD system. The system consisted of a capacitively coupled reactor operating at 13.56 MHz. The upper showerhead electrode was coupled to the rf generator via a matching impedance network. The inter-electrode spacing was about 4 cm and the diameters of both electrodes were about 16 cm^2. The gas flow-rates of SiH_4 (99.999% purity) and H_2 (99.999% purity) were fixed at 0.4 sccm and 8 sccm respectively maintaining the SiH_4 to H_2 ratio at 1:20 and the deposition pressure at 0.4 mbar throughout the deposition process. These samples were prepared using different rf powers of 15, 20, 40, 80, 120 and 160 W.
The infrared transmission spectroscopy were done on these films using a Perkin Elmer System 2000 Fourier transform infrared (FTIR) spectrometer with a scanning range of 400 to 4000 nm. The film thickness was determined using the Tolansky technique. X-ray diffraction measurements were performed using a Siemens D5000 x-ray diffractometer at a glancing incidence of 5° and a scattering angle of 10 to 80°. The average crystallite size was then determined using the Scherrer's equation [6]. The Raman spectra of the films were recorded using a Renishaw System 2000 Raman Spectrometer. The spectra were deconvoluted into three components, a sharp Lorentzian peak at ~520 cm^{-1}, an intermediate Gaussian peak at 490 to 500 cm^{-1} and a broad Gaussian peak at ~480cm^{-1}. The crystalline volume fraction, F_c and the grain boundary volume fraction, F_{gb} were determined from the integrated intensities of these peaks using formulas used in similar works [7].

RESULTS AND DISCUSSIONS

The variation of the deposition rate of the nc-Si:H thin films deposited on c-Si substrates with rf power is shown in Figure. 1. The deposition rate shows three regions of increments: a steep increase for the films deposited between 15 W and 40 W (region 1), a stable deposition rate for the films deposited between 40 W to 120 W (region 2) and a slow increase in deposition rate for the films deposited at 120W and 160 W (region 3). In region 1, the rf power actively dissociates the SiH_4 molecules producing radicals which actively promotes secondary reactions resulting in the steep increase in the deposition rate. In region 2, the rf power actively dissociates both SiH_4 and H_2 molecules resulting in the dominant presence of H radicals at the growth surface which initiate H etching effects. The H etching effects reduce the deposition rate resulting in the insignificant increase in the deposition rate in this region. In region 3, total dissociation of the reactive gas reduces secondary reactions and H etching effects. This increases the deposition rates but the resulting films are highly disordered as the dominant deposition precursor SiH_3 which result in a highly ordered film structure are significantly reduced.

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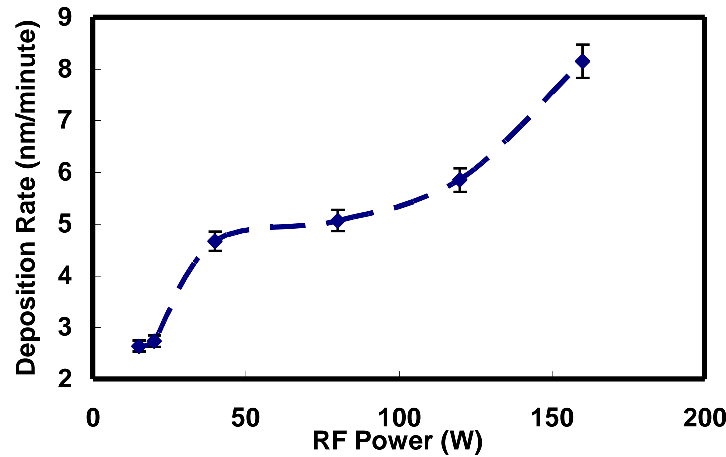

Figure. 1: Variation of deposition rate of nc-Si:H thin films with rf power

The bonded H content in the films was determined from the integrated intensity of the Si-H wagging band at 630cm^{-1}. A plot of the variation of the bonded H content in the film with rf power is shown in Figure. 2. The H content is highest for films prepared at rf powers of 15 W and 80 W.

Figure. 3 shows the variation of the microstructure parameter in the film with rf power. This parameter was determined from the ratio of the integrated intensity of the Si-H stretching absorption band at 2000 cm^{-1} to the sum of the integrated intensities of this absorption band and the Si-H_2 stretching absorption band at 2090cm^{-1}. This plot shows that this parameter increases significantly to a high value for the films deposited at the highest power of 120 W and 160 W indicating a more disordered film structure as compared to the other films.

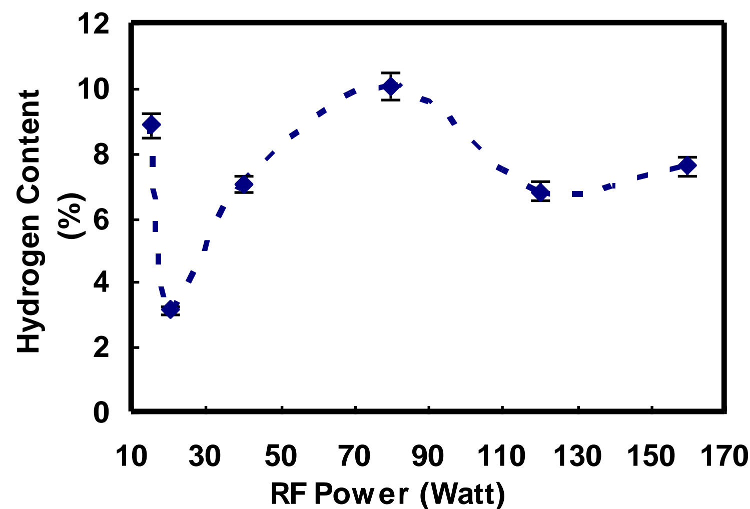

Figure. 2: Variation of bonded H content in the nc-Si:H thin films with rf power.

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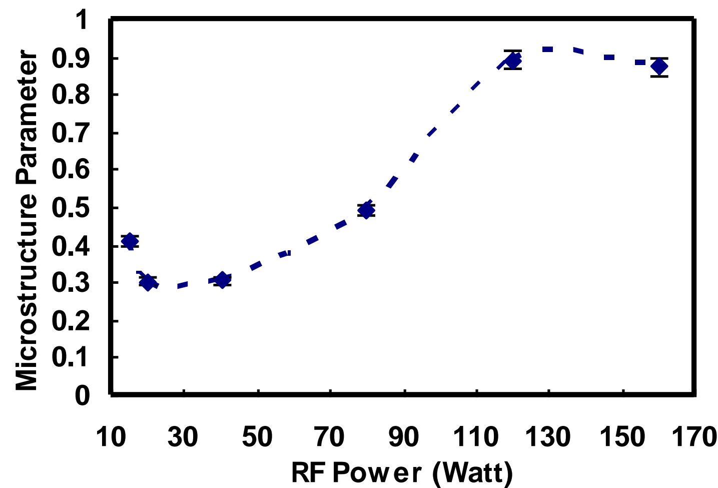

Figure. 3: Variation of microstructure parameter in the nc-Si:H thin films with rf power.

The diffraction peaks for nc-Si films usually appear at scattering angles of 28.5^o, 47.5^o and 56.2^o corresponding to the Si (111), (220) and (311) reflections respectively. For these films, both the (111) and (220) planes exist but the preferred orientation is the (111) plane. The crystallite size in nc-Si:H film is estimated from the (111) diffraction peak (the dominant orientation for all the films) by using Scherrer's equation and the variation of the crystallite size with rf power is plotted in Figure. 4. In the low rf power region, the crystallite size increases to a maximum at rf power of 40 W and decreases to a minimum for the films deposited at rf power of 80 W. A second maximum is observed for the film prepared at rf power of 120 W.

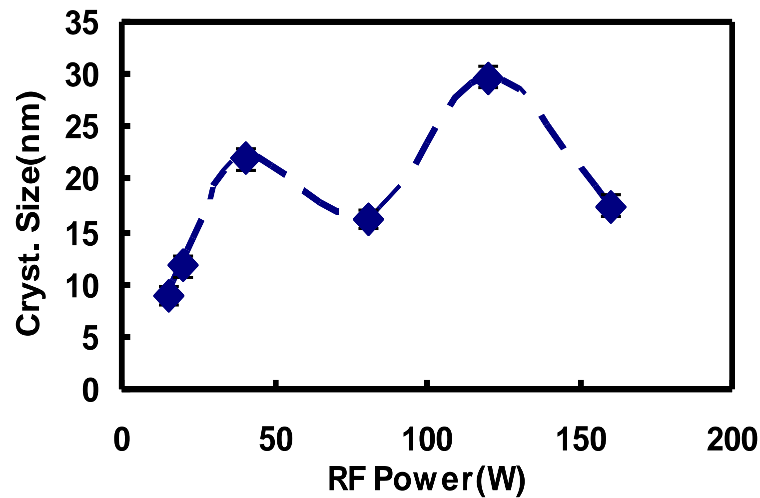

Figure. 4: Variation of crystallite size in the nc-Si:H films with rf power.

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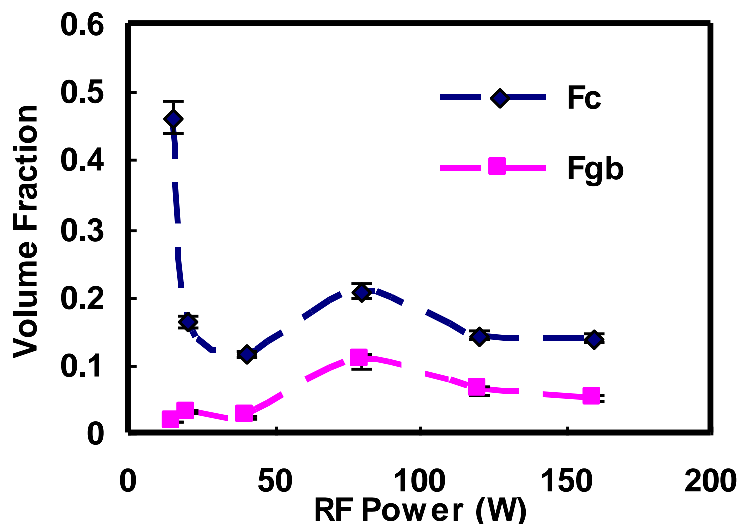

Figure. 5: Variation of crystalline volume fraction, F_c and grain boundary volume fraction, F_{gb} with rf power.

The Raman spectra of nc-Si:H for the samples studied in this work show a broad amorphous peak at 480 cm^{-1} and is dominant these films. A sharp nanocrystalline peak protrudes from this broad amorphous peak at 520 cm^{-1} for all films except for the film prepared at the highest rf power of 160W. This peak is most significant in the film prepared at the lowest rf power of 20W. The crystalline and grain boundary volume fractions versus rf power plots are shown in Figure. 5. The crystalline volume fraction is highest for the film deposited at the lowest rf power and shows another maximum for the film deposited at rf power of 80 W but the magnitude is significantly lower. The grain boundary volume fraction shows a single maximum for the film deposited at rf power of 80 W. The films with the higher crystallinity (rf power of 15 W and 80 W) appear to have smaller crystallites. Low ion bombardment and H etching effects have significant contribution to the crystallinity in the nc-Si:H films.

CONCLUSIONS

The effect of rf power on the deposition rate, H content, microstructure parameter and structure of nc-Si:H thin films deposited by our own home-built rf-PECVD system were studied. The deposition rates showed dependence on rf power. Low rf power dissociates SiH_4 molecules only and produces low ion bombardment damage. H etching is induced for the films deposited at rf power between 40 to120 W and rf power above 120 W results in total dissociation of SiH_4 and H_2 molecules. The presence of nanocrystallite clusters in the film structures is most dominant in films deposited at the lowest rf power. Low ion bombardment damage is an important factor to be considered in producing nc-Si:H films with nano-sized crystallites and high crystallinity. At this low power, the H_2 molecules are not discharged but help cushion ion bombardment

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effects. Films with nanocrystallite size and high crystallinity are also produced at higher rf power if the H etching effect is dominant. High rf powers produce highly defective films with low crystallinity due to ion bombardment effects and total dissociation of reactive gas molecules.

ACKNOWLEDGEMENTS

This work is supported by the Ministry of Science, Technology and Innovation, Malaysia under IRPA research grant 09-02-03-0222 EA222 and PJP/PPF 2005 Research Fund F0210/2005B. The authors would also like to thank Mr. Adam Menhat from MDC Department ShinEtsu for micro-Raman experiment.

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