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Optimization of intrinsic hydrogenated amorphous silicon deposited by very high-frequency plasma-enhanced chemical vapor deposition using the relationship between Urbach energy and silane depletion fraction for solar cell application

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ABSTRACT

Intrinsic hydrogenated amorphous silicon (i-a-Si:H) films were deposited by very high frequency (VHF) plasma enhanced chemical vapor deposition (PECVD) technique. It was found that there were three distinct deposition rate regions, when the deposition pressure and power were varied according to Paschen's law. The silane depletion fraction (SDF) is related to the reaction rates and the sticking probability of the radicals, which is smaller in the 1st region, where the SiH_3 radical is the dominant deposition precursor giving rise to higher film density and a low Urbach energy (~68 meV). The third region has higher SDF, where more SiH_2 radicals are generated resulting in a reduction in film density and increased structural disorder due to polyhydride formation. The good quality films obtained with the condition of the 1st region, showed low SDF at lower pressure and power, following Paschen's law. Some of these i-a-Si:H films were used to fabricate p–i–n type solar cells. The measured photo voltaic parameters of one of the cells are as follows, open circuit voltage (V_{oc}) = 800 mV, short circuit current density (J_{sc}) of 16.3 mA/cm^2, fill-factor (FF) of 72%, and photovoltaic conversion efficiency (η) of 9.4%, which may be due to improved intrinsic layer. J_{sc}, FF and V_{oc} of the cell can be improved further with optimized cell structure and with i-a-Si:H having a lower number of defects.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) and hydrogenated microcrystalline silicon (μc-Si:H) are commonly used in p–i–n type thin film solar cells because they can be deposited on various substrates. The research and development of a-Si:H based solar cell now aim towards mass production and cost reduction [1–3].

Radio frequency (RF) plasma enhanced chemical vapor deposition (PECVD) is one of the most popular industrial methods for the production of a-Si:H films. Although a uniform layer thickness is usually obtained at low deposition temperature, the films deposited by conventional 13.56 MHz RF PECVD method have low conductivity, low deposition rate and high hydrogen content [4]. To enhance the throughput of the PECVD process, a high deposition rate for the a-Si:H film is required. The electrical and optical properties of a-Si:H are known to be determined by its deposition conditions [4]. The growth of good quality a-Si:H thin films requires high hydrogen dilution of silane (SiH_4) during its deposition. An alternative deposition method is the 60 MHz (VHF) PECVD. The VHF PECVD offers the advantage of an enhanced gas dissociation rate, which results in a deposited film that is more stable. Additionally, during the VHF PECVD deposition, the self-bias, and therefore the ionic bombardment of the film growing surface, are reduced compared to the RF deposition, with a consequent reduction in structural damage and improvement of thin film quality [5].

The current understanding of plasma and film growth kinetics postulates that for a good device quality film, the neutral SiH_3 radicals should dominantly take part in the film growth at a low plasma power and low pressure [6]. However, SiH_3 radicals are about 90% of the total radical flux that is incident on the film growing surface. Since the surface of the growing film in a typical PECVD system is highly passivated by atomic hydrogen, a large fraction of the incoming SiH_3 radicals leave the film growing surface due to its lower sticking coefficient, or as the saturated molecules SiH_4 and Si_2H_6 which result from surface-catalyzed reactions.

Deposition of good quality i-a-Si:H thin films depend upon deposition conditions such as gas ratio, power, pressure, substrate temperature, and inter-electrode distance. The aim of this study is to obtain good quality i-a-Si:H thin films for solar cells, by the VHF PECVD technique. Low silane depletion fraction (SDF) was obtained through optimized plasma parameters. The influence of plasma power and pressure on the deposition rate, chemical, structural and electrical properties of i-a-Si:H thin films prepared in a VHF PECVD reactor was studied.

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2. Experimental details

Intrinsic a-Si:H thin films were deposited by 60 MHz VHF PECVD on Eagle 2000 glass (5 cm × 5 cm, 0.63 mm-thick) and Si wafer substrates. The glass substrate was ultrasonically cleaned by dipping in acetone, isopropyl alcohol, and de-ionized water for 10 min. The a-Si:H films were deposited with thickness of about 0.3 μm, by glow discharge decomposition of SiH_4 and H_2 mixtures. The deposition conditions used were 53.3 Pa pressure, 30 W VHF power, 50 sccm SiH_4 flow rate, 50 sccm H_2 flow rate, 20 mm electrode distance and 200 °C substrate temperature. Then, optimizations of power and chamber pressures were carried out.

In order to estimate the number of hydrogen bonds in Si–H, Si–H_2 and $(Si-H_2)_n$, forms Fourier transform infrared (FTIR) measurements were performed using an IR Prestige-21 spectrometer (Shimadzu, 7800–350 cm^{-1}). The 'microstructure parameter' (R*) is defined as $R^* = I_{2090}/(I_{2090}+I_{2000})$, where I_{2000} and I_{2090} are the integrated intensity of the FTIR absorption spectra centered around 2000 and 2090 cm^{-1} respectively. Spectroscopic ellipsometry (SE) (VASE®, J.A. Woollam, 240 nm < λ < 1700 nm) was used at an angle of incidence of 65°, in the spectral range of 240 nm to 1700 nm, to measure the thickness, refractive index, and absorption coefficient (α), of the i-a-Si:H films, from which the optical band gap (E_g) and Urbach energy (E_u) of the films were estimated. The surface roughness was estimated from the SE measurement using the Bruggeman effective medium approximation (B-EMA). For electrical measurements, Al coplanar electrodes (300 nm thick) were evaporated on the films that were deposited on the glass substrate. The electrical characteristics were studied using a programmable Keithley 617 electrometer in the temperature range of 25 to 125 °C and the dark conductivity activation energy (E_a) was estimated. Room temperature Raman spectroscopy (Ramboss 500i, Dongwoo optron, with 514.5 nm laser line) was used to study the changes in the crystallinity of the films.

The solar cells were fabricated on transparent conducting oxide coated glass (Asahi VU-Type) [7] and layers were deposited in cluster-type RF and VHF PECVD system. Each of the p-, i-, and n-type layers was deposited in separate chambers. The p-layers of the cells were boron doped hydrogenated amorphous silicon oxide (a-SiOx:H), while the i- and n-type layers were a-Si:H based. The deposition conditions of the solar cells are summarized in Table 1. The i-a-Si:H layer was deposited by VHF-PECVD, but the p-type and n-type layers were deposited by RF PECVD. The substrate temperature was fixed at 175 °C for p-type layer deposition and 200 °C for i- and n-type layer depositions. The SiH_4 concentrations, defined as $SiH_4/(SiH_4+H_2)$, were 95, 50 and 20%, the powers were 30, 20 and 50 W and the deposition pressures were 93.3, 26.7 and 26.7 Pa for p-type, i-type and n-type layers, respectively. For the p- and n-type layer depositions, the ratio of the B_2H_6 and PH_3 to SiH_4 was fixed at 2% and 1% respectively. The electrode separations of the PECVD system were set to be 60, 20 and 40 mm for p-, i- and n-type layer depositions, respectively. After deposition of the layers, the electrode at the back of the cell was formed with Ag and Al double layers, and evaporated through a mask (6 mm × 6 mm) for defining the cell area. A silver grid was applied at the front for good Ohmic contact. Reactive ion etching was carried out using SF_6 gas on the top side for mesa-etching. Finally, the a-Si solar cells were characterized by current–voltage (I–V) measurements under AM 1.5 illumination with 100 mW/cm^2 light intensity at a temperature of 25 °C.

Table 1
Deposition conditions for the p-, i-, n-type layers of the solar cell.

Layer of the solar cell	Gas flow rate (sccm)					Pressure (Pa)	Power (Watt)	T_s (°C)	Thickness (nm)
	SiH_4	N_2O+He	H_2	B_2H_6	PH_3				
p	5	3.0 + 27	99	0.1	0	93.3	30	175	15
i	50	0	50	0	0	26.7	20	200	450
n	30	0	120	0	30	26.7	50	200	25

3. Results

3.1. Deposition rate (R_d)

Fig. 1(a) shows the deposition rate of the i-a-Si:H thin films at different pressure and power. A steep rise in R_d has been observed at around 53.3 Pa deposition pressure. There are three regions distinguished by pressure range, as 26.7–60.0 Pa, where the R_d increases with deposition pressure (1st region), 60.0–9.0 Pa, where the growth rates remain almost unchanged (2nd region), and 90.0–106.7 Pa, where the R_d decreases (3rd region) at lower power, but increases at higher power. Similar features were reported earlier [8–11], which is thought to be due to the transition from the α to γ′ regime. An increase in the R_d of the film and a change of the film properties were observed near the transition from the α and γ′ regime. During the deposition of the i-a-Si:H films, the dissociation of silane and hydrogen takes place as H, SiH, SiH_2, SiH_3, and $(SiH_2)_n$. Gas phase polymerization can be another reason for the limitation of deposition rate, which results in powder formation at the wall of the deposition chamber, at a higher deposition pressure. In the 2nd region, the R_d increases with increasing pressure up to 66.7 Pa, attaining around 1 nm/s deposition rate.

Fig. 1(b) shows the power dependence of the R_d at constant pressures. Each region shows different trends. The generation of silane

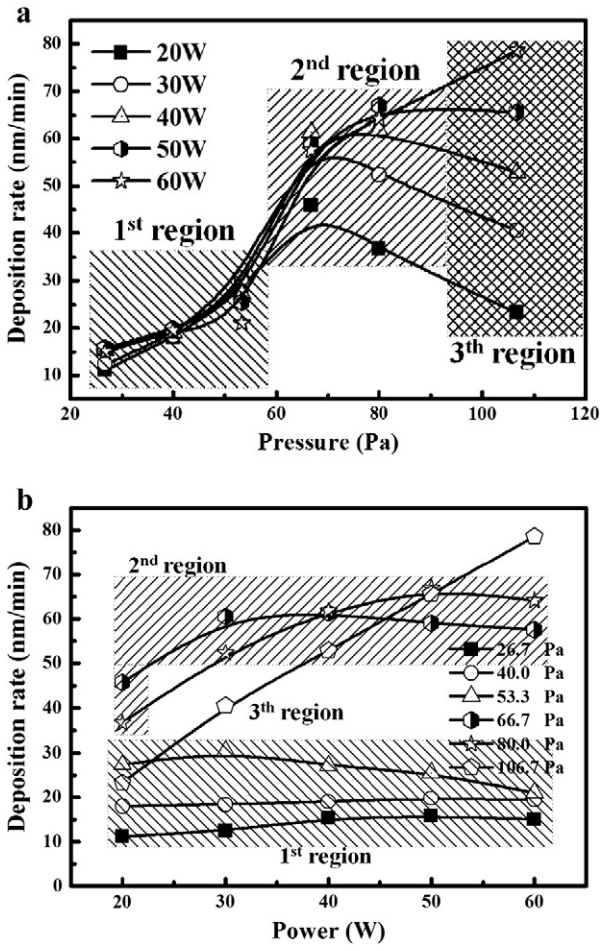

Fig. 1. (a) Deposition rate of i-a-Si:H films with pressure at different plasma power: 20 W (squares), 30 W (circles), 40 W (triangles). 50 W (hexagons), 60 W (stars). (b) Dependence of film deposition rate with RF power at different deposition pressure: 26.7 Pa (squares), 40.0 Pa (circles), 53.3 Pa (triangles). 66.7 Pa (hexagons), 80.0 Pa (stars), 106.7 Pa (pentagons).