Electrical Properties of Boron and Phosphorus Doped μc-Si:H Films using Inductively Coupled Plasma Chemical Vapor Deposition Method for Solar Cell Applications

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Hydrogenated microcrystalline silicon(μc-Si:H) films were prepared using inductively coupled plasma chemical vapor deposition(ICP-CVD) method, electrical and optical properties of these films were studied as a function of silane concentration. And then, effect of PH_3 and B_2H_6 addition on their electrical properties was also investigated for solar cell application. Characterization of these films from X-ray diffraction revealed that the conductive film exists in microcrystalline phase embedded in an amorphous network. At PH_3/SiH_4 gas ratio of 0.9×10^{-3}, dark conductivity has a maximum value of ~18.5 S/cm and optical bandgap also a maximum value of ~2.39 eV. Boron-doped μc-Si:H films, satisfied with p-layer of solar cell, could be obtained at $\sim10^{-2}$ of B_2H_6/SiH_4.

Keywords : ICP-CVD, Microcrystalline Si, Solar cell, Boron, Phosphorus, Conductivity

1. INTRODUCTION

Hydrogenated microcrystalline silicon(μc-Si:H) is believed to be a mixed phase consisting of small (10~500 Å) crystallites in an amorphous silicon(a-Si:H) matrix. It has a higher doping coefficiency than a-Si:H for both n and p type doping, and is therefore considered to be a very promising material for contacts in thin film devices such as solar cells, thin film transistors(TFTs), and light emitting diodes(LEDs)[1,2]. It has higher absorption coefficients in the visible region of wavelength (600~800 nm) than a-Si:H, and so a higher short-circuit current could be obtained when it is used as active layer in solar cell[3-5]. In addition to the above advantages, it does not exhibit degradation of photoconductivity due to light irradiation[4]. Despite these advantages, it is not often used as the layer in thin film devices, due to the large defect density between the small crystalline grains.

Recently μc-Si:H solar cells with the high efficiency of over 10 % have been obtained[6]. The difference in the open circuit voltage(V_{oc}) is only 10 % even though the difference in grain size by several orders of magnitude. This is attributed to the hydrogen passivation of the grain boundary defects and the suppression of the recombination rate at the grain boundaries. For the growth of μc-Si:H films using CVD methods, one of the most significant things is to form the films at a much lower temperature(200~400 °C).

Recently, most equipments for depositing amorphous silicon and μc-Si:H films are based on capacitively coupled plasma reactor method. However, it may have inherent drawbacks such as low deposition rate and damages on growing film caused by high energy particles. It has been reported that there are various techniques of improving the deposition rate and avoiding the damage of plasma, as very high frequency CVD(VHF CVD), hot wire chemical vapor deposition(HWCVD), and remote PECVD[7-9]. Among these techniques, An inductively coupled plasma chemical vapor deposition(ICP-CVD) has some advantages in the deposition at low temperatures because of its high plasma density of $\sim10^{12}$ cm^{-3}, a good uniformity without external magnets and less ion bombardment on the surface. It has also the potentials in depositing μc-Si:H films with large area. However, it is

difficult to form microcrystalline silicon phase using ICP CVD because that couldn't be worked at high process pressure.

The purpose of this study is to report in detail on developing an ICP-CVD method to deposit boron and phosphorus doped μc-Si:H films, applicable to the solar cells. Deposition process with the variations of gas ratio (H_2/SiH_4) was performed in sequence. For boron and phosphorus doped μc-Si:H films, bandgap and electrical properties with the variation of doping gas ratio were also reported.

2. EXPERIMENTS

2.1 Preparations

The undoped and doped μc-Si:H films were deposited on the p-type (100) oriented CZ c-Si (1-20 Ω·cm, 500 μm) wafers and Corning 1737 glasses with 2 cm×2 cm size using an ICP CVD system. Substrates were cleaned for pre-deposition. A pure silane (SiH_4, 99.99 %, Suzuki Shokan Co. Semicondutor Grade) was used as the source gas. 97 % hydrogen diluted diborane (B_2H_6) and 99 % hydrogen diluted phosphine (PH_3) were used as doping gas. The working pressure was maintained constant by using an automatic throttle valve. For the removal of the absorbed water vapor in the samples, a substrate holder and deposition chamber was baked for 30 minutes at 250 °C and 50 °C, respectively. Inductively coupled electrical field produced from an antenna coil, which located on the dielectric plate, generates the plasma. The distance between shower head and substrate holder was about 23 cm. The total flow rate of hydrogen and silane gas was fixed at 100 sccm. In this experiments, first the $SiH_4/(SiH_4+H_2)$ gas ratio was varied in the range of 0.016~0.045 (the H_2/SiH_4 dilution ratio in the range 61.5~21.2). Second, the B_2H_6/SiH_4 and PH_3/SiH_4 gas ratio were varied in the range of 1.08×10^{-2}~2.7×10^{-3} and 0.9×10^{-3}~3.6×10^{-3}, respectively.

2.2 Characterization

In order to assess properties of the deposited films, firstly thickness and optical bandgap were measured by a surface profiler (Nanofocus, μsurf) and a spectroscopic ellipsometer (Jobin Yvon, UVISEL). Dark conductivity (σ_d) and photoconductivity (σ_{ph}) were measured to investigate the electric properties of the deposited films. For σ_d and σ_{ph} measurements, two metal contact pads (99.999 % aluminum, 3 mm long, separated by 1 mm) were evaporated through a shadow mask on as-deposited films in order to form an ohmic contact. To investigate σ_d and its activation energy(E_a) in the samples, a probe station system(Suss Microtec, Probeshield), which are is consisted of semiconductor characterization system (Keithley 4200), LCR meter(Agilent E4980A) and

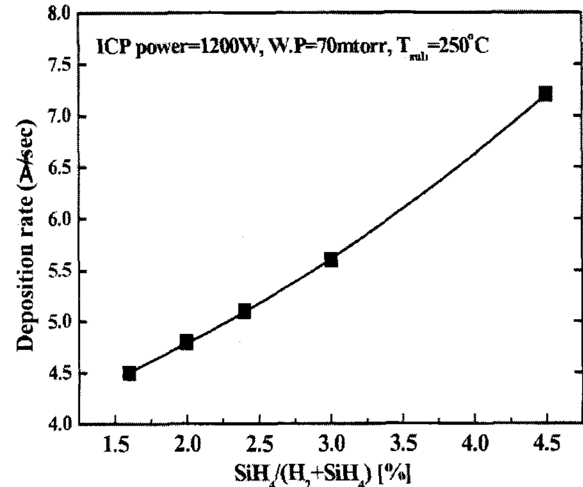

Fig. 1. Deposition rate of intrinsic μc-Si:H films as functions of silane concentration.

temperature controller, was used. σ_{ph} measurements were obtained under the conditions of air mass(AM) 1.5, 100 mW/cm^2 and 25 °C. The system consists of three parts: (1) solar simulator (Wacom, WXS-105H), (2) I-V measurement part (HP4140B pAmeter/DC voltage source) and (3) light intensity measurement part (Epplex Lab. Inc. Thermopile). Finally, X-ray diffraction system (PANalytical, X'pert Pro MRD) was used to assess the structural properties of films.

3. RESULTS AND DISCUSSION

3.1 Intrinsic μc-Si:H films

The deposition rate is determined by the flux density of the film precursors such as SiH_x radicals, and the generation rate of radicals G_r is given by the following expression,

$$G_r = n_e\ v_e\, N_g\, \sigma_d \tag{1}$$

where, n_e and v_e are the density and velocity of energetic electrons, respectively, with a kinetic energy higher than the dissociation threshold of the source gas molecule such as SiH_4. N_g and σ_d are the density and the dissociation cross section of the source gas molecules.

Figure 1 shows the relation between silane concentration and deposition rate of μc-Si:H at 1200 W of ICP power, 70 mtorr of working pressure, and 250 °C of substrate temperature conditions. It can be found that there is linear relation due to increase of silane molecule. In general, as the dissociated silane molecule increase, it contributes to grow grain in films.

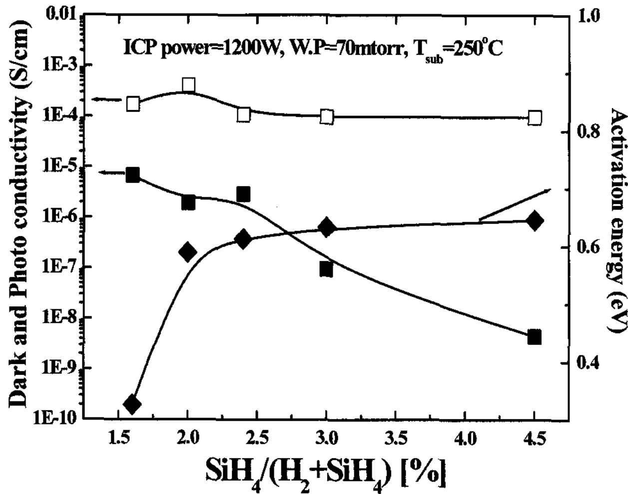

Fig. 2. Electrical conductivity and activation energy of intrinsic μc-Si:H films as functions of silane concentration.

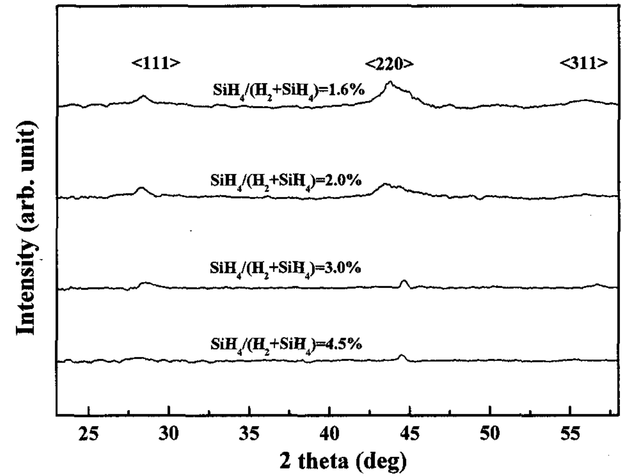

Fig. 3. X-ray diffraction spectra of intrinsic μc-Si:H films with the variation of silane concentration. There may be three peaks corresponding <111>, <220>, and <311>.

The electric conductivity (S/cm) and activation energy(eV) of dark-conductivity as functions of silane concentration(SiH_4/H_2+SiH_4)shown in Fig. 2. The measurement of the temperature dependence of the dark conductivity is used to evaluate the activation energy of the dark conductivity, which gives a good approximation of the position of the Fermi level in μc-Si:H films. The temperature dependence of the dark conductivity $\sigma_d(T)$ is described as[10]

$$\sigma_d(T) = \sigma_o \exp(-E_a/kT) \quad (2)$$

where σ_o is a conductivity prefactor, T the absolute temperature and k Boltzmann's constant. From the slope of the Arrhenius plot, which in this case is the relationship between $\log(\sigma_d(T))$ and 1/T, the activation energy is determined.

As SiH_4 contents decrease, the deposition of amorphous silicon phase is suppressed due to etching by ion bombardment. At the same time, crystalline silicon phase is enhanced due to the increase of atomic hydrogen density. When the silane concentration was over 3.0 %, amorphous silicon film was obtained by annihilation reaction ($H+SiH_3 \rightarrow SiH_4+H_2$) due to the increase of SiH_3 density. As a results, the condition of electrical properties (σ_d : ~10^{-7} S/cm, σ_{ph}: ~10^{-4} S/cm) and the activation energy (0.55 eV), satisfied with properties of intrinsic μc-Si:H, was obtained at 2 % of silane concentration, respectively.

In order to assess the structure of μc-Si:H films, XRD data with increase of silane concentration were measured in Fig. 3. Three peaks corresponding to <111>, <220>, and <311> could be observed at the SiH_4/H_2+SiH_4 ratio of 1.6 ~4.5 %. As the gas ratio decreased to 1.6 %, three peaks may be more dominant. However, the shifted (220) peak were observed due to imperfection transition between microcrystalline and amorphous phase. Compared to films using other method such as VHF-CVD and HWCVD, the poor crystallinity and grain size were shown. It is clear that pressure range of ICP-CVD method should be higher over 0.3 torr. Unfortunately, the maximum working range of this apparatus used in this experiment is 0.1 torr. As shown in Fig. 2, electrical properties, satisfied with intrinsic μc-Si:H films, could be obtained despite of unsatisfied crystalline phase.

3.2 Boron and phosphorus doped μc-Si:H films

As shown in Fig. 4, σ_d and optical bandgap of the deposited films as functions of B_2H_6/SiH_4 gas ratio has almost same tendency. Optical bandgap(E_g) of μc-Si:H film could be obtained from the wavelength dependence of its absorption coefficient(α).

The E_g is determined by extrapolating $[\alpha(E)n(E)E]^{1/1+p+q}$ versus the photon energy E to $\alpha(E)$, for $\alpha \geq 10^3$ cm^{-1}:

$$[\alpha(E)n(E)E]^{1/1+p+q} = B(E-E_g) \quad (3)$$

where $\alpha(E)$ is the absorption coefficient, n(E) is the refractive index of a-Si:H. The p and q are constants related to the shape of the band edges and B is a constant.

If the density of states has a square-root energy dependence near the band edges, as is commonly the case in crystalline semiconductors (p=q=1/2), equation 1 describes the so called *Tauc Plot* and the corresponding the *Tauc gap*[11]. The pseudo refractive index <n(E)>

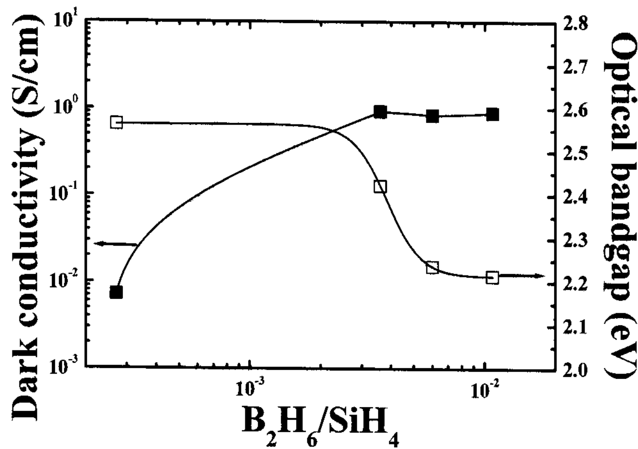

Fig. 4. Change of dark conductivity and optical band-gap with variable of diborane concentration.

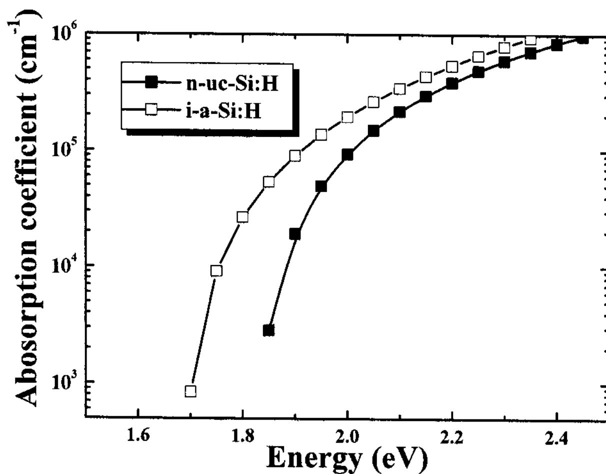

Fig. 5. Comparison of absorption coefficient between intrinsic a-Si:H and phosphorus doped μc-Si:H film.

and extinction coefficient <k(E)> of sample could be obtained by SE and then, experimental data could be modeled by a Tauc-Lorenz dispersion law to extract material characteristics[12]. Dark conductivity has the best value of 0.089 at doping ratio of 0.0108 and decrease in the case of $2.7E^{-4}$ since boron doping efficiency becomes small. As the B_2H_6 doping ratio increases, the optical band-gap deceases to 2.21 eV. It is attributed to reaction of excessive boron. Namely, excessive boron as a defect in films may exist to increase of localized state density in forbidden gap.

The absorption coefficient of phosphorus doped μc-Si:H films, compared to intrinsic a-Si:H, is presented in Fig. 5. The crystalline fraction of n-μc-Si:H films is higher than that of a-Si:H. Absorption occurs predominantly by transitions between the extended states of the valence and conduction bands.

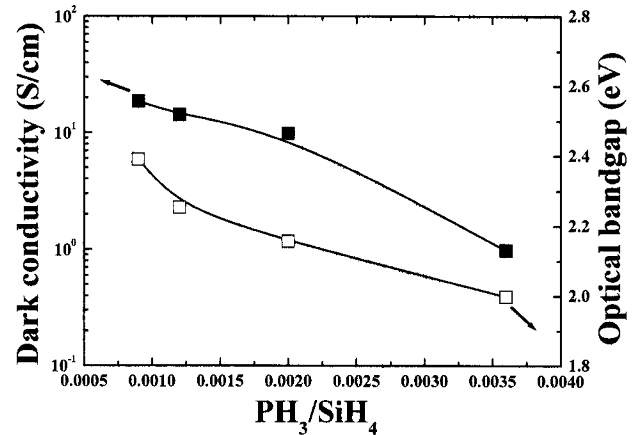

Fig. 6. Change of dark conductivity and optical bandgap with variable of phosphine concentration.

As shown in Fig. 6, dark conductivity has a best value of ~21 S/cm and optical band-gap also a maximum value of ~2.39 eV at PH_3/SiH_4 gas ratio of 0.9×10^{-3}. As PH_3/SiH_4 gas ratio more increases, both dark conductivity and optical band-gap decrease. From the results it can be known that phosphorus doping in μc-Si:H films to a certain extent shows rather good for high conductivity and wide band-gap. Even if the PH_3/SiH_4 gas ratio was increased from 0.9×10^{-3} to 3.6×10^{-3}, the σ_d of n-μc-Si:H layer was decreased form 18.5 to 9.8×10^{-1} S/cm. This is also attributed to extra phosphorus atoms acts as defects not dopants.

4. CONCLUSION

Hydrogenated microcrystalline silicon(μc-Si:H) films were prepared using inductively coupled plasma chemical vapor deposition(ICP-CVD) method, electrical and optical properties of these films were studied as a function of silane concentration. And then, effect of PH_3 and B_2H_6 doping concentration on their electrical properties were also investigated for solar cell application. Characterization of these films from X-ray diffraction revealed that the conductive film consists of microcrystalline Si-phases embedded in an amorphous network. At PH_3/SiH_4 gas ratio of 0.9×10^{-3}, dark conductivity has the best value of ~18.5 S/cm and optical bandgap also the best value of ~2.39 eV. Boron-doped μc-Si:H films, satisfied with p-layer of solar cell, could be obtained at ~10^{-2} of B_2H_6/SiH_4. Consequently, Undoped and doped μc-Si:H films with the variation of gas ratio using ICP-CVD method could be obtained for solar cell applications.

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