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Isochronal Studies of a-Si:H Crystallization and the Performance of it's Schottky Barriers

Hydrogenated amorphous silicon films (α-Si:H) were crystallized employing a metal induced crystalline (MIC) technique. Structural changes during annealing these films at 300^0C for different periods (0-300minutes) were obtained by XRD. Al was used as a metal induced crystalline for α-Si:H produced by ultra high vacuum (UHV) plasma enhanced chemical vapor deposition (PECVD). XRD shows that crystallization of the interacted α-Si:H film underneath Al initiates at 300^0C for 15 minutes. A complete crystallization was obtained after annealing for 60 minutes. A gold dot was evaporated onto α-Si:H films, which annealed for different periods to form Schottky barriers. Electrical properties of Au/α-Si:H were calculated such as the ideality factor, n, barrier height, Φ_B, donor concentration, N_D, and the diffusion voltage, V_d, as a function of the annealing time of α-Si:H films. All these parameters were carried out through the current voltage characteristics (J-V) and the capacitance voltage measurements (C-V). The results were presented a discussed on the basis of XRD performance and the thermionic emission theory.

Keywords: hydrogenated amorphous Si, crystallization, PECVD, Schottky barrier, electrical properties

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1. Introduction

Solar cells based on α-Si:H are the most popular and low cost option for applications ranging from consumer products to building integrated power generation systems. However, the power conversion efficiency of an all α-Si:H cells are limited due to the excessive defects [VOHRA et al]. It is well known that solid phase crystallization (SPC) is the most common method used to crystallize amorphous silicon (α-Si) and the SPC temperature of α-Si can be lowered by the addition of a materiel such as Al, Ni, Cu, Ag. [VOHRA et al.; YOON et al.; AL-DHAFIRI et al. (a); AL-DHAFIRI et al. (b); AL-DHAFIRI et al. (c); RADNOCZI et al.; BIAN et al.].

There is interest in metal/ α-Si:H Schottky diode structures because of their sensitivity to visible light and their use as photodectors. Due to their ease of fabrication metal/ α-Si:H test structures are extensively used to study the optoelectronic properties of intrinsic α-Si:H films for solar cells application [FORTMAN et al.; HELLER et al.]. To avoid the problems associated with α-Si:H, it can be converted to c-Si:H by deposition a metal onto α-Si:H and then, annealed at relatively low temperature [HAQUE et al. (1994); HAQUE et al. (1996)]. Crystallization of α-Si:H in contact with Al has been observed to initiate as low as 180^0C

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[HAQUE et al. (1994)]. Hentzell et al. have reported that Al interacts with α-Si at 150^0C by forming an Al-rich metastable silicide, which crystallizes at 300^0C and breaks up at 350^0C to yield polysilicon [HAQUE et al. (1994)]. Herd et al. found that Al causes α-Si to crystallize at 340^0C. For α-Si:H, however, Tsai et al. reported that crystallization occurs at 250^0C. Schropp et al. observed that Al /α-Si:H interaction is initiated at 200^0C and crystallization occurs at 250^0C.

Schottky diodes, is a useful structure to extract the information regarding the bulk α-Si:H. Simeonov and Kafedjiiska reported a correlation between the barrier height Φ_B and the ideality factor, n, and the temperature at which the experiment carried out. While Song et al. explained the changes of Φ_B to the inhomogeneous over the M-S interface; Tung reported that the value of the ideality factor, n, changes with the temperature change only for a special shape and distribution of inhomogeneous Schottky barrier subareas.

In this article, the crystallization of α-Si:H by aluminum induced crystallization method was investigated at 300^0C for a different annealing time, 15, 30, 60, 120, 180, 240, and 300 minutes. An Au/α-Si:H Schottky barriers were made and the electrical properties such as the ideality factor (n), the diffusion voltage(V_d), donor concentration(N_D), the barrier height(Φ_B) were reported as a function of the annealing time of the α-Si:H substrate.

2. Experiment

N-type <100> crystalline silicon wafers were used as a substrate for α-Si:H film deposition. The substrates were first cleaned using standard cleaning methods. An intrinsic α-Si:H films of about 5000^0A were deposited on the substrate using an ultra high vacuum (UHV) plasma enhanced chemical vapor deposition (PECVD) system. The deposition parameters were fixed as follows, the base pressure 6×10^{-8} torr, the temperature 250^0C, the pressure 500 mtorr and power density 50 $mWcm^{-2}$. A phosphorous to silane volume ratio of 1% was used for all films. After the deposition, the samples were allowed to cool to room temperature in vacuum. The chamber was then filled with dry nitrogen and the samples were immediately transferred to thermal evaporation system where an Al film of approximately 3000^0A was deposited at room temperature. The samples were then, annealed at 300^0C in the range of 0-300minutes.

XRD was used to determine the lattice and structure of silicon films. This was done using a Siemens D5000 with Cu Kα radiation of average wavelength 1.54056^0A. It was operated with target voltage, 30V and current, 20mA. The diffraction patterns were from $2\theta = 0$ to $2\theta = 100$. The capacitance voltage (C-V) measurements were carried out at 1MHz using a Model 410 Princeton Applied Research Capacitance bridge. The dark current-voltage (J-V) measurements were obtained point by point.

3. Result and Discussion

Figure 1 shows the x-ray diffraction spectra of an α-Si:H films annealed at 300^0C for 0, 15, 30, and 60 minutes, taken after removing the Al. As expected, no crystalline silicon peaks were recorded for as-made films. Two very weak peaks observed from those films, which annealed for 15 minutes (fig.1B). One is at $2\theta = 28.5^0$, which is assigned as Si (111) and the other is at 2θ = 47⁰ from Si (220). These two peaks indicate the beginning of the formation of polycrystalline film. When the films were annealed for 30 minutes, another peaks were observed at 2θ = 56⁰ which assigned as Si (311) (fig. 1C). The relative peak intensity of Si (111) and Si (220) are becoming stronger for this period of annealing. These results indicate that the annealed samples for 60 minutes has the better crystallinity and that it has more peaks at 2θ = 69⁰, 2θ = 76.5⁰ and 2θ = 88⁰ corresponding to Si: (400), Si (331) and Si (422) respectively (fig. 1D). All the measured peaks were observed very sharp, high intensity and easily identifiable when the annealing time is increased to 120, 180, 240, and 300 minutes. The XRD spectra for these periods of annealing are not included in figure 1.

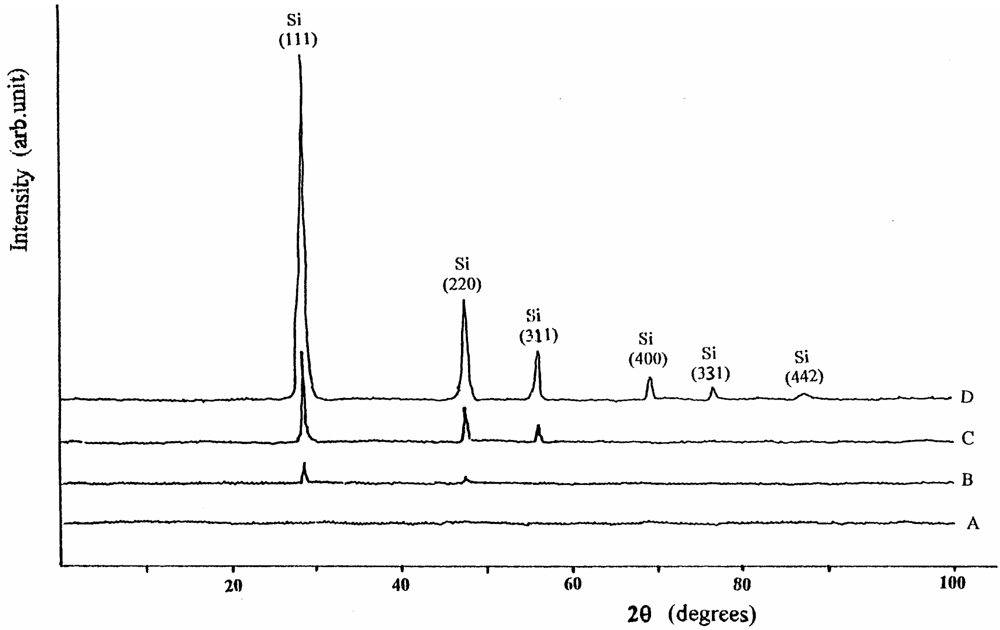

Fig. 1: XRD spectra of the α-Si:H films annealed at 300 °C for 0 (A), 15 (B), 30 (C), 60 (D) minutes

From figure 1, it is clear that the solid phase crystallization temperature is 300⁰C for 15 minutes and complete solid phase crystallization was achieved at the same temperature for 60 minutes. It is worth to mention that the spectra taken after removing the Al film do not show any Al peaks, which indicates the absence of metallic Al in the polycrystalline silicon film formed by metal-induced crystallization (MIC) of α-Si:H. Metal-induced crystallization of α-Si:H has been proposed to explain this behavior. HIRAKI [(1980); (1986)] explains, in his model, screening model, almost all-experimental results. In this model, for a metallic layer thicker than a critical value, the Si covalent bonds at the interface become weak and induce an exothermic reaction due to the release of interfacial energy. The metal-silicon interface region melts for a short time and cools down rapidly leading to the formation of an amorphous alloyed interface. The composition of this layer is close to that a metal-silicon alloy with lowest melting point or deepest eutectic point (TDE). When the film is annealed, small grains of crystal start to grow. The formed silicide is the most stable near TDE in the phase diagram. In the case of Al/α-Si:H, HAQUE et al. [(1994); (1996)] have reported in their model, the rich silicide formed during the initial stage of the interaction is expected to reject all Al metal during crystallization . The possibility of some of the rejected Al segregating at the grain boundaries is thus ruled out the XRD measurements. It is also shown that the Si nuclei formed at the Al/α-Si:H interface and that growth proceeded within the Al layer until adjacent grains in pinged [NAST and WENHAM]. The overall crystallization process resulted in the exchange of layer positions and the formation of a continuous poly-Si film consisting of grain up to tens of microns in size depending on the annealing temperature [NAST and WENHAM].

After removing the Al film, a gold dot was evaporated on the as-made and annealed α-Si:H substrate at 300^{0}C for 15, 30, 60, 120, 180, 240 and 300 minutes to complete the Schottky diodes. Figure 2 shows the dark J-V characteristics of Au/α-Si:H Schottky barriers fabricated on these films. As expected, an ohmic behavior was obtained for those diodes, which formed on as-made α-Si:H films. It is clear, from this figure that by increasing the annealing time of the α-Si:H substrate, the Au/α-Si:H devices show a good diodes behaviors with a reduction in the reverse bias leakage. This diodes behavior confirms that the conversion of the α-Si:H to polycrystalline silicon by (MIC). Although a drastically increase of the conductivity, as can be seen from figure 2, the series resistance of the devices getting high by increasing the time of the annealing of the α-Si:H films. The deviation of the J-V curves towards the x-axis is normally taken as a sign of increasing of series resistance.

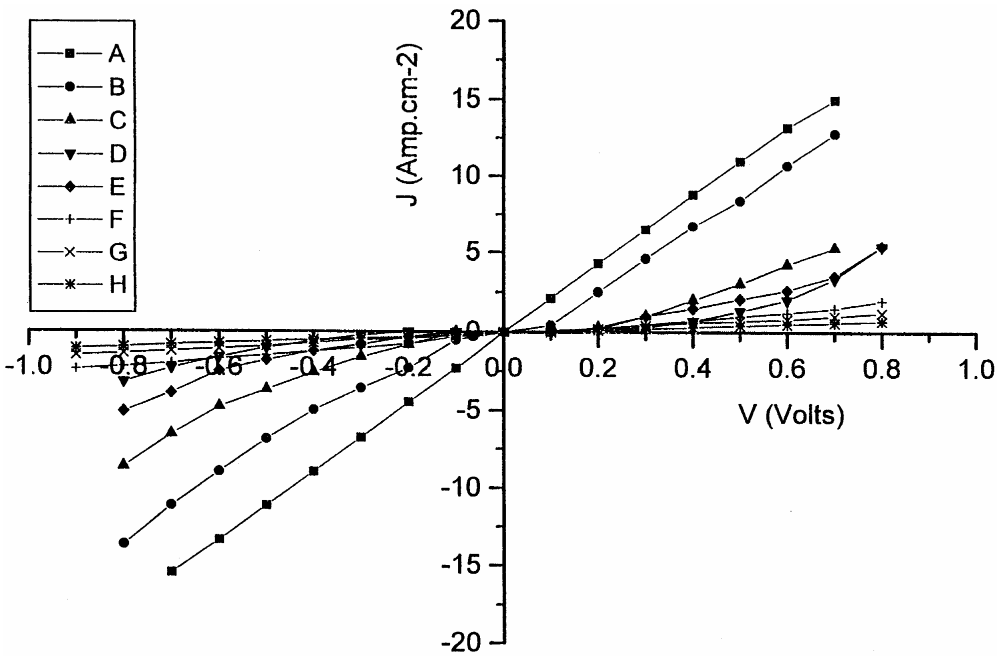

Fig. 2: The dark J-V characteristics for a Schottky barrier fabricated on α-Si:H substrate after annealing at 300°C for 0 (A), 15 (B), 30 (C), 60 (D), 120 (E), 180 (F), 240 (G) and 300 (H) minutes

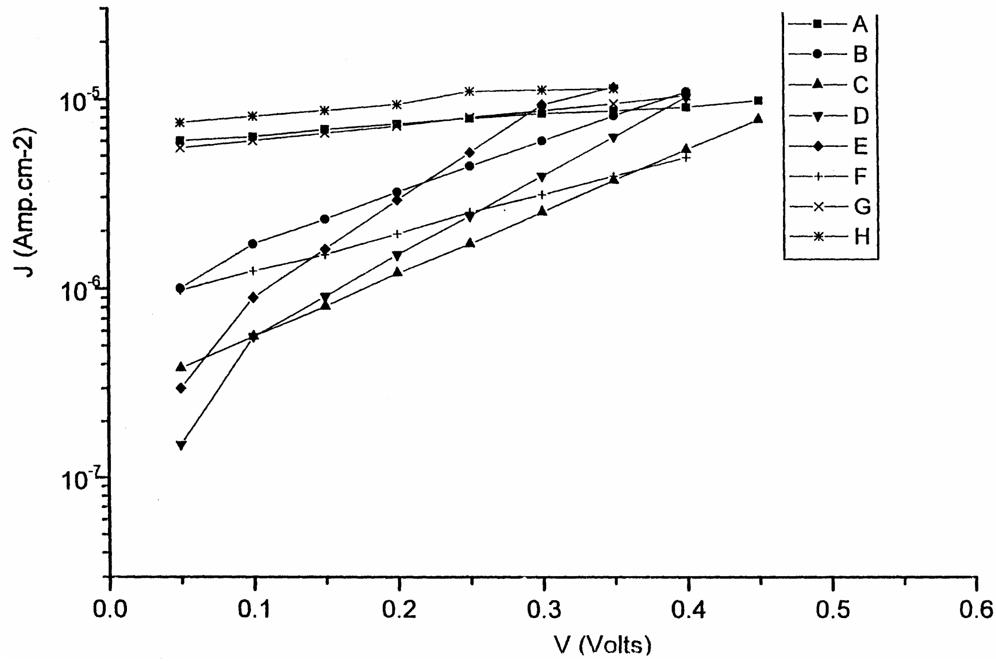

Fig. 3: The forward J-V characteristics for a Schottky barrier fabricated on α-Si:H substrate after annealing at 300°C for 0 (A), 15 (B), 30 (C), 60 (D), 120 (E), 180 (F), 240 (G) and 300 (H) minutes

Figure 3 shows typical room temperature dark forward J-V characteristics for Au/α-Si:H diodes fabricated on a substrate α-Si:H annealed for different periods. The current density in an ideal Schottky diodes, calculated by thermionic emission theory is given by RHODERICK;

$$J=J_0 \, [\exp (qV/nkT)-1] \qquad (1)$$

Where,

$$J_0=A^* \, T^2 \, \exp (- qV/kT) \qquad (2)$$

is the current density in the Schottky diode extrapolated to V=0. Here, J is the forward current density, J_0 the saturation current density, q the electron charge, V the bias voltage, k the Boltzmann constant, T the temperature, n the ideality factor, A^* the Richardson constant and Φ_B the Schottky barrier height. In terms of the unidimensional model of the thermionic emission theory, the ideality factor must remain close to unity independently of the applied bias and the measurement temperature [RHODERICK], leading to a linear J-V semilogarthmic characteristic in the bias range where the series resistance effect can be neglected and for V> 3kT/q. The values of the ideality factor, n, were calculated by using equation 1. For the Schottky diodes fabricated on a substrate annealed for 60 and 120 minutes, thermionic emission appears to be the dominant current mechanism (n= 1.06 and 1.13 respectively). In some diodes the ideality factors were found equal to 1.35, 1.87, 2.26, for diodes fabricated on a substrates annealed for 30, 15, 180 minutes respectively. This is pointing a complex current mechanism. Higher ideality factors were obtained for the rest of the devices, which fabricated on as-made and annealed of a α-Si:H films for and 300 minutes showing a more complex current mechanism. The barrier heights can be determined from J-V curves by using equation 2. These values were summarized in table 1. The compressions between these values and the other deduced from C-V measurements are discussed in the next paragraph.

Table 1:

Duration of annealing (minutes)	Ideality Factor, n	Barrier Height, $\phi_{B\,(J-V)}$, eV	Barrier Height, $\phi_{B\,(C-V)}$, eV	Donor Concentration, N_D, (cm^{-3})	Diffusion Voltage, V_d (Volt)
0	10.71	0.492	------	0.01×10^{15}	-----
15	1.85	0.570	0.420	1.1×10^{15}	0.18
30	1.35	0.591	0.525	1.7×10^{15}	0.33
60	1.06	0.662	0.630	2.4×10^{15}	0.29
120	1.23	0.730	0.665	2.1×10^{15}	0.57
180	2.62	0.620	0.680	1.9×10^{15}	0.48
240	4.16	0.752	0.690	2.2×10^{15}	0.60
300	4.35	0.705	0.695	2.3×10^{15}	0.65

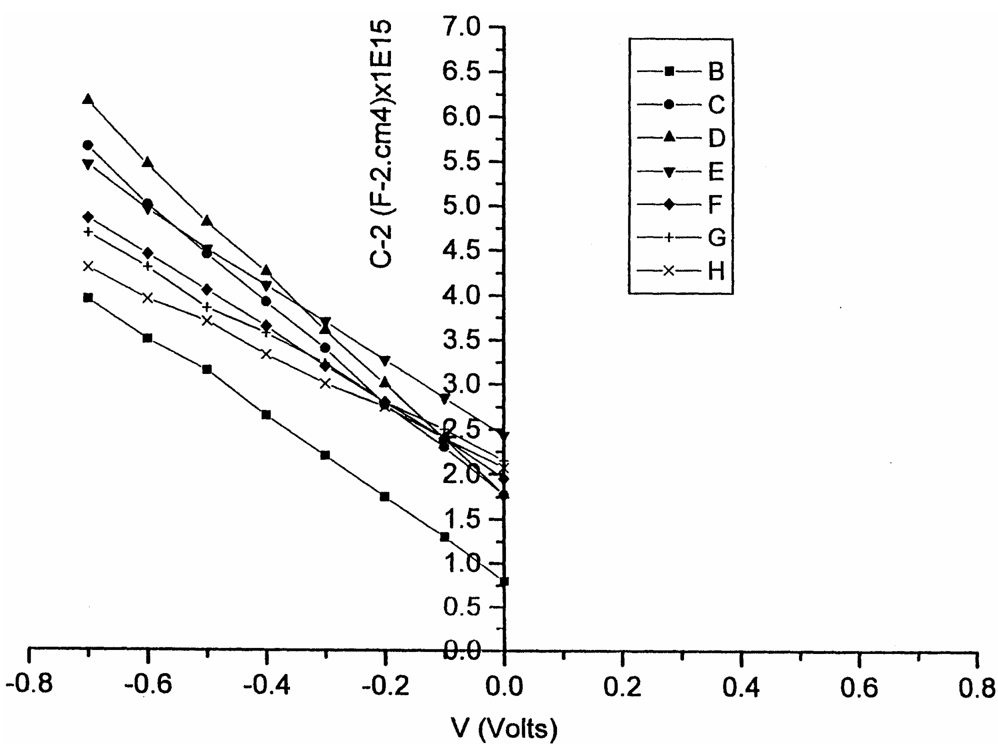

Fig. 4: The C-2-V characteristics for a Schottky barrier fabricated on α-Si:H substrate after annealing at 300°C for 15 (B), 30 (C), 60 (D), 120 (E), 180 (F), 240 (G) and 300 (H) minutes

The capacitance voltage (C-V) measurements for all of the Au/α-Si:H diodes were carried out as a function of annealing time of the α-Si:H substrate. The C^{-2} were plotted versus the reverse bias V_r and shown in figure 4. As expected, [RHODERICK], these graphs are straight lines with an intercept V_d on the horizontal axis. The diffusion voltages (cutoff voltage) were found to be in the range of 0.18-0.65V. Calculated values of donor concentration, N_D, for Schottky diodes fabricated on a substrate annealed at 300^0C for different periods varied between 0.01×10^{15}- 2.4×10^{15} cm^{-3}. A barrier height of Au/α-Si:H was measured from figure 4 and it was 0.42, 0.525, 0.630, 0.665, 0.680, 0.690, and 0.695 for those devices made on an annealed α-Si:H at 300^0C for 15, 30, 60, 120, 180, 240and 300 minutes respectively. Some of these values were found to be close to the other values reported by Simeonov and Kafedjiiska. The measurements for the devices formed on as-made substrate could not carry out. As can be seen, the barrier height was increased dramatically after annealing the substrate. The improvement of the barrier height is due to the conversion of the amorphous phase to crystalline phase. AL-DHAFIRI et al. (d) found that, the grain sizes getting bigger with a uniform distribution after annealing of the Al/α-Si:H. The higher relative values are also probably connected with a higher surface donor defect concentrations obtained on these samples. It is known, that the values of the barrier heights obtained from J-V measurements are not accurate and some times in disagreement with those, which obtained from C-V measurements according to Goodman and Cowley and Heffine . It might also be due to the fact that Schottky barrier theory for C-V behavior dos not account for the presence of localized states and the resulting modification to the slope and intercept of the C^2-V plots. The variation of V_d, N_D, $\Phi_{B\ (J-V)}$, $\Phi_{B\ (C-V)}$, with the duration of the Al/ α-Si:H substrate annealing is summarized in table 1.

4. Conclusions

α-Si:H films were fabricated by ultra high vacuum (UHV) plasma enhanced chemical vapor deposition (PECVD) system. XRD shows that crystallization of the interacted α-Si:H film underneath Al initiates at 300^0C for 15 minutes. Different periods of time were applied (0-300minutes). A complete crystallization was obtained after annealing for 60 minutes. Electrical properties were investigated through current voltage (J-V) characteristics and capacitance voltage (C-V) measurements of Au/α-Si:H. A correlation was obtained between the electrical properties such as the ideality factor, n, barrier height, Φ_B, donor concentration, N_D, and the diffusion voltage, V_d and the annealing time of α-Si:H substrates.

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