Thin silicon films ranging from amorphous to nanocrystalline obtained by Hot-Wire CVD

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Abstract

In this paper we present results on silicon thin films deposited by Hot-Wire CVD at low substrate temperature (200°C). Films ranging from amorphous to nanocrystalline were obtained by varying the filament temperature from 1500 to 1800°C. A crystalline fraction of 50% was obtained for the sample deposited at 1700°C. The results obtained seemed to indicate that atomic hydrogen plays a leading role in the obtention of nanocrystalline silicon. The optoelectronic properties of the amorphous material obtained in these conditions are slightly poorer than the ones observed in device-grade films grown by Plasma-Enhanced CVD due to a higher hydrogen incorporation (13%).

Keywords: Amorphous silicon, nanocrystalline silicon, HWCVD.

1. Introduction

Hot-wire CVD (HWCVD) has shown to be a promising technique for the deposition of silicon thin films for photovoltaics and large area electronic applications [1]. This technique allows the deposition of device quality material at high deposition rates with low hydrogen contents and improved stability under light soaking [2]. Although typical deposition temperatures required to obtain device grade materials in HWCVD are higher than the ones required in Plasma-Enhanced CVD (PECVD), several studies have been done in order to lower the deposition temperature so that low cost substrates such as glass, plastic or even polymer foils can be used.

Thin silicon films ranging from amorphous (a-Si:H) to nanocrystalline (nc-Si:H) can be obtained by HWCVD by properly tuning the deposition conditions. This transition has been achieved by varying different technological parameters such as hydrogen dilution [3], substrate temperature [2] and process pressure. In this work we focus on the transition under the variation of the filament temperature (T_f). Structural, optical and electrical properties of several samples deposited at low substrate temperature and different T_f are presented.

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2. Experimental

Thin silicon films (0.7-0.8 μm thick) were deposited onto Corning 1737 glass and Si(111) in a HWCVD reactor described elsewhere[4]. The dissociation of the gases was achieved by means of a tantalum filament heated at temperatures in the range of 1500 to 1800°C. A process pressure of $3.8 \cdot 10^{-2}$ mbar, a substrate temperature of 200°C and a pure silane flow of 4 sccm were used.

Crystalline fraction (X_c) of the films was deduced from Raman Spectroscopy, following [5]. Hydrogen content and the microstructure factor (R^*) [6] were obtained from Fourier Transform Infrared (FTIR) spectrometry. Photothermal Deflection (PDS) and Optical Transmission Spectroscopies were used to obtain the band gap (E_g) and the Urbach energy (E_u). Dark conductivity vs. temperature and Steady State Photoconductivity (SSPC) measurements were performed in order to obtain the activation energy (E_a), mobility-lifetime product ($\mu\tau$) and dark conductivity at 33°C (σ_d).

3. Results and discussion

3.1 Structural properties

The transition from a-Si:H to nc-Si:H has been observed under appropriate tuning of the filament temperature. All the samples exhibited a deposition rate of approximately 4 $\text{\AA}/\text{s}$, indicating a complete dissociation of the gases at the filament surface regardless the T_f in the studied range.

The structural properties of the samples (X_c and R^*) as a function of T_f can be seen in Fig. 1(a). Samples obtained at $T_f \geq 1750^\circ\text{C}$ showed a clear nanocrystalline character with X_c greater than 90%. On the other hand, the samples grown at $T_f \leq 1650^\circ\text{C}$ showed amorphous behaviour. For T_f around 1700°C, X_c in the range of 50% were obtained, which showed an intermediate regime between both structures. The change in crystallinity seems to be induced by an increase of atomic hydrogen produced at the surface of the wire at higher T_f .

Fig. 1 Structural properties (a) and optical properties (b) for samples deposited at different filament temperatures. In Fig. 1(b) the nanocrystalline and amorphous gap energies are presented for the sample in the transition zone (see text).

R^* values in the order of 0.1 have been obtained for the amorphous samples. This reflected the high density of the material. Nanocrystalline samples presented values of R^* higher than 0.4, increasing with higher T_f .

3.2 Optical properties

The E_g and E_u are presented in Fig. 1(b). Both energies exhibited the same behaviour for T_f below 1650 °C, showing a clear amorphous character with an average E_g of around 1.7 eV and an E_u of 70 meV. This last value is higher than that expected for device quality material [6]. This fact can be related to the high hydrogen concentration in the samples, which is in the range of 12-13% for the amorphous samples and around 7 % for the nanocrystalline ones. A reduction of the hydrogen content in the samples requires changes in the technological parameters such as an increase in the substrate temperature [2] or hydrogen dilution [3]. At temperatures above 1750°C, the optical properties exhibited a nanocrystalline behaviour of the samples, in agreement with the structural properties. In the transition zone, both amorphous and nanocrystalline absorption edges were observed because the material consisted of a mixture of both phases, each being dominant in a different energy range. Fig 1(b) shows the gap energies of both absorption edges for the transition sample.

3.3 Electrical properties

Dark conductivity at 33°C, E_a and $\mu\tau$ as a function of T_f are shown in Fig. 2. E_a was calculated by fitting the Arrhenius plot in the range of high temperatures (150-80°C), where the conduction through extended states is dominant.

Fig. 2 Electrical properties as a function of the filament temperature

At temperatures lower than 80°C, a bending in the Arrhenius plot of σ_d of the amorphous samples appeared. The exponential behaviour in this range of temperatures corresponds to a lower E_a and a prefactor $\sigma_0 \approx 1$ S/cm which has been attributed to thermal hopping in band tail states [7]. The values

of σ_d shown in Fig. 2 are reasonable for device-quality a-Si:H, in spite of a slight increase in σ_d for the sample deposited at 1650°C. The $\mu\tau$ remains almost constant for all the amorphous samples although its value is slightly lower than the typical ones reported in the literature for device-quality a-Si:H [6]. When we take into account all these facts, it seems to be more difficult to obtain device-grade material at low substrate temperatures in HWCVD than it is in PECVD.

In the transition zone, the electrical properties of the material seem to be dominated by the nanocrystalline contribution even though a X_c of 50% is obtained from the Raman spectra.

Nanocrystalline samples showed a mid-gap character with a slight increase in E_a and decrease in $\mu\tau$ when increasing the filament temperature. This could be related to the incorporation of a deep defect level related to impurities coming from the wire as has been observed in recent studies [8].

4. Conclusion

Changes in the wire temperature made it possible to control the crystalline fraction of the samples while keeping the deposition rate constant.

Amorphous silicon obtained at low substrate temperature (200°C) by HWCVD has a higher hydrogen content than standard PECVD. This fact causes broader tail bands. As a consequence, a higher Urbach energy of the optical absorption edge and a bending in the Arrhenius plot are observed.

Nanocrystalline silicon samples with a high crystalline fraction were obtained without hydrogen dilution of the silane feed. The increasing wire temperature produced a decrease of the mobility-lifetime product which is attributed to slight metallic contamination coming from the wire.

Acknowledgments

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