Thermal effects on LPCVD amorphous silicon

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Abstract

The effects of thermal annealing on amorphous silicon deposited using low-pressure chemical vapour deposition (LPCVD) are presented in this paper. The amorphous silicon film is being subjected to different annealing conditions ranging from 600 to 900 °C for a varying period of 30 to 90 min holding time in nitrogen ambient. X-Ray diffraction (XRD) shows that crystallization of amorphous silicon to poly-silicon starts to occur after 30 min of thermal cycle at 600 °C. Atomic force microscope (AFM) has been used to study the surface roughness and grain size of the films after different annealing times and temperatures. The nanocrystalline grains result in photoluminescence behavior. Stress measurement, using curvature analysis, shows that the stress magnitude reduces with decreasing annealing temperature and time. This is likely due to stress relief during grain growth and crystallization at higher temperatures. The detailed study of the structural, morphology and property changes in amorphous silicon upon annealing will be presented.

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1. Introduction

Low pressure chemical vapor deposition (LPCVD) polycrystalline silicon (poly-Si) has been intensively studied because of its important applications in the ultra-large scale integrated (ULSI) technology as gate materials for field effect transistors, as emitters in bipolar transistors and as part of interconnects. Surface roughness, grain size and trap density of active poly-Si layers are very important variables which affect the properties and functionalities of the films [1–3].

Amorphous silicon (α-Si) continuously gains interest in nanoelectronics mainly because of its small homogeneous grains and photoluminsous properties. α-Si can potentially replace poly-Si as gate electrode in sub 50 nm transistors mainly because of its smaller grains and lower temperature of deposition. Besides the use as control gates and floating gates, α-Si is also investigated as an important material for its application in nano-structures and for thin film transistors (TFTs). Re-crystallized α-Si TFTs are used to form simple integrated circuits, such as static shift registers, that have enormous potential for other applications.

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Deposition studies of silicon films conducted at 500 °C<T<600 °C revealed that α-Si was in a metastable state with respect to its crystalline allotrope. The deposition temperature strongly influenced the crystallization rate [3]. From previous studies, LPCVD α-Si was not uniformly flat but had its own structure consisting of many amorphous grains [4,5]. The sizes of these amorphous grains changed in accordance to the deposition conditions because of the change in nucleation and growth rates. If the film nucleation rate was relatively fast compared to the film growth, the silicon film was composed of many small amorphous grains. Conversely, if the film growth rate was relatively fast compared to the film nucleation rate, the silicon film was composed of a few large amorphous grains.

It was also found that an LPCVD amorphous film has two different phases, amorphous-I and amorphous-II. The amorphous-I was a well-known phase in which the amorphous grains grow in size as the deposition temperature reduces. The amorphous-II was a phase in which the amorphous grains decrease in size as the deposition temperature falls. The kinetics of LPCVD film growth was governed by the relative magnitude of the surface reaction to the gas-phase mass transfer.

This paper reports the effects of thermal cycles on LPCVD deposited α-Si with assessment made on the grain orientation,
grain size, grain growth, surface roughness, morphology and stress measurement. Optical properties such as photoluminescence are also reported with the recrystallization into nanocrystalline Si.

2. Experimental

A 1000 Å SiO₂ was thermally grown on p type (100) Si substrates. Si thin films were deposited by LPCVD at 550 °C, 475 mTorr on these oxidized Si substrates. The as-deposited Si films were of 1000 Å thick as measured using an ellipsometer. The samples were subjected to various annealing temperatures of 600, 700, 800 and 900 °C for holding time of 30 min, 60 min, 90 min and 4 h. Samples were placed into a horizontal tube furnace for annealing with a constant injection of 10,000 sccm N₂ gas into the tube. Ramping time was set at 4 °C/min. After the annealing temperature was reached, a stabilization time of 5 min was used for each annealing process. The annealed silicon films were characterized using AFM, XRD, film stress measurement (FSM) and photoluminescence (PL). The PL measurements were performed at room temperature using the 488 nm line of an argon laser as the excitation source. Stress measurement was done using wafer curvature analysis with the reference film at the oxidized silicon substrate.

3. Results and discussion

Fig. 1 shows the XRD spectra of the α-Si films after various annealing times. After annealing at 600 °C for 30 min, the presence of XRD peaks at 28.5°, 47.5° and 56.3° correspond to Si (111), (220) and (311), respectively. All the annealed samples show a strong preferential orientation of (111) plane. Similar results are obtained for samples annealed at 700, 800 and 900 °C. Crystallization of α-Si is shown to have started to occur after annealing at 600 °C for 30 min. As the annealing temperature increases, the intensity of the XRD peaks increases which shows the increment in the degree of crystallization in the silicon film. Detailed analysis shows that the peak width of the XRD peaks reduces and indicates a growth in the crystallites diameter as a function of temperature and time. This will be further studied in detail using AFM analysis.

Fig. 2 shows the comparison of average grain sizes of α-Si estimated from AFM analysis after annealing at different conditions. The grain size of α-Si increases as the annealing time increases for each temperature. The percentage increment in grain size is greater as a function of temperature compared to annealing time. It is observed that at 900 °C, the grain size seems to reach a saturation grain size quickly when subjected to annealing time for more than 1.5 h. It is clearly seen that all the annealed films possess nanocrystalline grains.

Fig. 3 shows the comparison of the roughness value obtained from AFM analysis of α-Si after annealing at different conditions. It is observed that as annealing time increases, the surface roughness reduces. For a lower annealing temperature, the surface roughness of the recrystallized α-Si is reduced to a larger extent as compared to higher thermal annealing temperature of 800 and 900 °C. At 900 °C, the surface...
roughness remains fairly constant after annealing for more than 1.5 h. For α-Si deposited on an underlying oxide layer, the crystallites were found mainly at the oxide–amorphous interface [5]. During thermal annealing, the amorphous-to-crystalline transition occurs in columnar growth; in an upward direction from the substrate. The crystallization transition will be completed when the amorphous–crystalline interface reached the upper surface of the films, which can occur after a short time anneal at 900 °C or prolonged anneal at low temperatures.

Fig. 4 shows the comparison of the stress values extracted from wafer curvature measurement of α-Si after annealing under different conditions. The stress in α-Si generally decreases when the annealing temperature and time increases. Possible reason could be the strain relaxation related to grain size increment when annealing temperature and time increases. The amount of grain boundaries is decreased upon grain growth and results in less stress accumulation. This is because grain boundaries are generally of high energy, disordered and stress regions, grain growth will be able to relieve stress in these microstructure.

The optical properties of the nanocrystalline Si grains are depicted in Fig. 5(a) to (d) showing the PL spectra of α-Si annealed at 600, 800 and 900 °C for various annealing times. It is observed from the figures that the PL peaks range from 670 to 695 nm and the PL intensity increases as annealing time is prolonged. The peaks also slightly redshifted as anneal time increases. It can be seen that a small luminescence appeared after 700 nm. This range of luminescence peaks may be attributed to the microstructures of the Si [6], or due to the existence of some localized oxidized states of Si in the samples that limits the emitted wavelength [7]. The width of the peaks generally remained fairly constant as temperature and/or time increased. According to the carrier quantum confinement theory, an increase in the crystallite size would result in a redshift of the PL peaks. This is due to the reduction of the band gap in the Si nanocrystals.

It has been shown that the grain size of α-Si is largest after annealing at 4 h at various annealing temperatures (Fig. 3). Nevertheless, it was observed that as annealing time increased, the PL intensity seemed to saturate after 60 min at 600 and 800 °C annealing. This could be due to the fact that the grain dimensions after 4 h annealing became too large to observe quantum confinement effects. On the other hand, in Fig. 5(d), the PL spectra shows substantial increase in intensity after 4
Annealing at 900 °C; this is probably due to the more homogeneous grain size distribution and low roughness of the film.

There is ample evidence in this study that shows the presence of nanometer size crystallites. Findings from AFM and XRD measurements have demonstrated the presence of crystallites in the range of 1.5 to 4.5 nm giving red luminescence. In crystalline Si, the radiative recombination rate was very low because the radiative process involved the participation of a third particle, such as a phonon, which is capable of providing momentum conservation during recombination [8]. As a result, non-radiative recombination predominated and the quantum efficiency is typically <0.0001% at room temperature. This indicates that the red PL band is associated with the presence of nanocrystalline Si grains.

4. Conclusion

This work studies the effects of annealing on LPCVD deposited α-Si at different temperatures and times. It is found that crystallization has started at low annealing temperature of 600 °C. The percentage increment in grain size is greater as a function of temperature as compared to annealing time. The grain size seems to reach saturation when subjected to annealing time for more than 1.5 h at 900 °C. The surface roughness of the recrystallized α-Si is reduced to a larger extent at lower temperatures as compared to higher annealing temperature of 800–900 °C, while the grain size increases as a function of annealing temperature and time. The thin film stress measurement shows that the stress in α-Si thin film reduces with temperature and time. Possible reason could be that during grain growth, the number of grain boundaries is decreased which results in less stress accumulation.

The nanocrystalline grains result in photoluminescence behavior. The PL intensity is found to increase with annealing time of α-Si and results in a redshift in the PL peaks. As indicated in the carrier quantum confinement theory, an increase in the crystallite size would result in a redshift of the PL peaks, which is due to the reduction of the band gap of the Si nanocrystals.

References