Effects of deposition and annealing conditions on the structure and electrical properties of LPCVD silicon thin films

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Deposition temperature and annealing conditions have pronounced effects on the structure and electrical properties of LPCVD silicon thin films. Films grown at 580°C are amorphous whereas those grown at 620°C are microcrystalline. All thin films are subjected to phosphorous diffusion followed by different annealing treatments. Annealing of amorphous films at 1000°C results in large grains with no favoured orientation and with a relatively high mobility value. Annealing treatment at 1000°C of the microcrystalline sample results in moderate grain growth with a relatively low mobility which presumably is due to some favoured grain orientation. © *2000 Kluwer Academic Publishers*

1. Introduction

The ease of fabrication of polycrystalline silicon (or polysilicon) thin film over large areas, when compared to single crystal silicon films, has led to their extensive usage in Very Large Scale Integrated (VLSI) circuit technology for various application, e.g., MOS gates, load resistors in memory cells and inter connects, etc., [1]. Polysilicon thin films deposited by low pressure chemical vapour deposition (LPCVD) of silane (SiH_4) are generally used for above mentioned applications [1, 2]. Attempts are being made for direct use of LPCVD polysilicon films for active semiconductor layers on thin film devices such as diodes [3, 4] and transistors [5–8] for large area applications.

In order to apply these technologies effectively, a sound understanding of the relationship between microstructures, e.g., grain size, texture, etc., and electrical properties of polysilicons is necessary. Joubert *et al.* [2] reports that for films deposited in silane partial pressure range of 2×10^{-4} to 1 torr and the temperature range of 580 to 700°C, the pressure is a determining factor for crystallite size, texture, and surface roughness. For a constant temperature, the crystallite size decreases with the increase in pressure. No texture is observed at a very low pressure, but at an intermediate pressure the <110> preferred orientation is observed in the film. Voutsas and Hatalis [9] studied the structure of the polysilicon films deposited in the temperature range of 530 to 600°C and in the pressure range of 2 to 300 m Torr. They infer that deposition temperature is not the only parameter that determines the structure of the as-deposited films. Deposition pressure and source gas dilution are also important factors. Some work has been carried out on the effect of deposition temperature on the mobility of crystallized and partially crystallized polysilicon thin films [10–12].

In this paper the effects of deposition temperature, film thickness, and annealing conditions on the crystal structure and the electrical properties of undoped and phosphorous doped LPCVD silicon thin films have been studied.

2. Experimental procedures

The silicon thin films were deposited by thermal decomposition of pure silane at 580 and 620°C substrate temperatures in an LPCVD system. Silicon gas flow rate was 40 sccm and deposition pressure was maintained at 250 m Torr. In all cases, the silicon films were deposited on the top of a layer of thermal SiO_2 (about 1900 Å thick) of amorphous structure grown on a silicon wafer (0.5–1Ω cm p - type). Thin films of two different thicknesses, 1000 and 3000 Å, were grown. Phosphorous doping for all samples was done by diffusion at 600°C for 10 minutes using $POCl_3$ as a dopant source; phosphosilicate glass was then removed by giving a dilute HF dip. The samples deposited at 620°C were annealed at 1000°C for 2 hours. In the case of sample

deposited at 580°C, one set of samples was annealed at 600°C for 48 hours followed by a high temperature annealing at 1000°C for 2 hours. All annealing treatments were carried out in the protective atmosphere of nitrogen.

Contacts for the measurements of resistivity and Hall mobility were made by evaporating aluminium at the edges of the square sample (1 cm × 1 cm). The resistivity was measured using Van der Pauw's four probe technique [13]. Hall mobility measurements were performed at the magnetic field of 0.14 tesla. Transmission electron microscopy (TEM) samples were prepared in a two-step process. At first, the substrate was thinned using 10 : 1 : 1 etchant of HNO_3, H_2O and HF, protecting the polyside from the etchant by coating with a negative photoresist. Then both sides were coated with the negative photoresist, and a tiny hole at the centre of the substrate-side coating was made using a needle point. Then the sample was etched in a 3 : 1 : 1 etchant of HNO_3, H_2O and HF until a tiny hole was formed in the sample. Photoresist was removed by boiling the sample in H_2SO_4. Samples were observed in a Philips CM12 STEM operated at 120 kV.

3. Results and discussion

The summary of the experimental results is presented in Table I. The crystal structures of the as-deposited silicon thin films are shown in column 4 of Table I. It is apparent that the transition between amorphous to crystalline state is occurring somewhere between 580 and 620°C deposition temperature. The 620°C as-deposited film is fully microcrystalline. Both 120 and 318 nm thick films behave in the same way. It is interesting to note that the amorphous films have few uniformly distributed nano-crystalline regions in it. These nanocrystallites act as the nucleus for the grains developed during subsequent heat treatment. A typical electron diffraction pattern from an amorphous silicon thin film is shown in Fig. 1.

All as deposited films were doped with phosphorous as described in the previous section. Then phosphorous doped silicon films were subjected to various heat treatments. The films of 120 nm thickness are discussed first. In the case of 620°C as-deposited microcrystalline film, a 1000°C for 2 hours heat treatment following phosphorus diffusion results in a grain size of 51.4 nm (sample A in Table I). The heat treatment temperature of 1000°C is quite high because the recrystallization temperature of silicon is about 0.4 Tm, where Tm is the melting point of silicon in absolute scale. A significant grain growth occurs above the recrystallization temperature. The 620°C as-deposited films are microcrystalline, and each crystallite in it has a size bigger than the critical nucleus size. Therefore, no further nucleation is required, and only the growth of the crystallites occurs during the 1000°C annealing treatment.

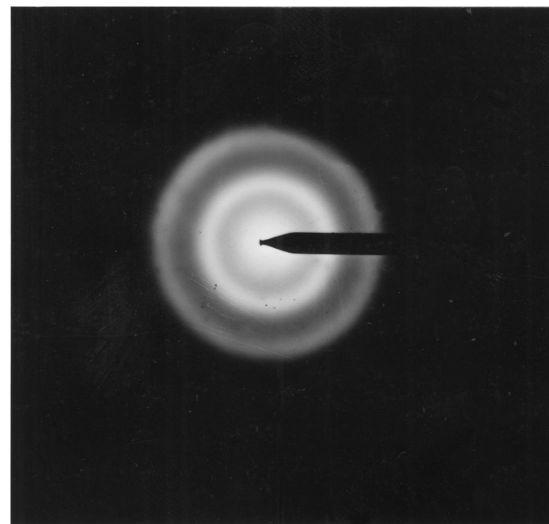


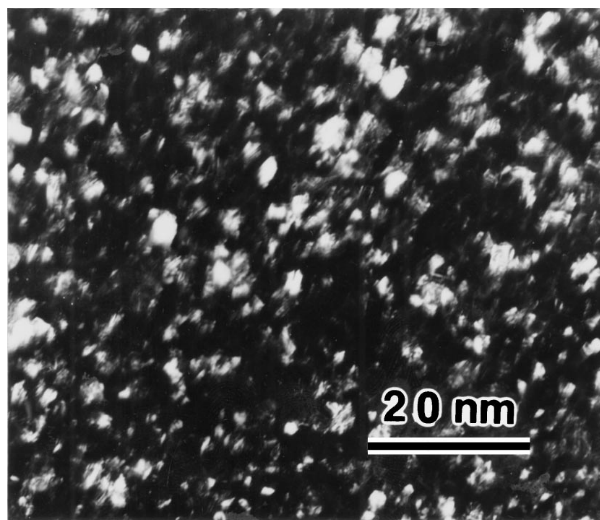
Figure 1 Electron diffraction pattern from the as-deposited amorphous silicon thin film (of 120 nm thickness) deposited at 580°C.

The 580°C as-deposited silicon thin film is of amorphous structure with localized regions having atomic arrangements close to that of the crystalline sample. These localized areas are in the nanometer size range, and they act as the nucleus during subsequent heat treatment process. The heat treatment at 600°C for 48 hours after the phosphorous diffusion results a grain size of 28 nm (sample B in Table I). The microstructure consists of both relatively large grain along with micro or nano-crystalline regions. Both temperature (600°C) and time (48 hours) are not sufficient enough for complete transformation of amorphous films to films consisting of only relatively large grains. When these samples are further heat treated at 1000°C for 2 hours, the grain size increases to 95.5 nm (sample C in Table I) from 28.0 nm. Such an increase is owing to the fact

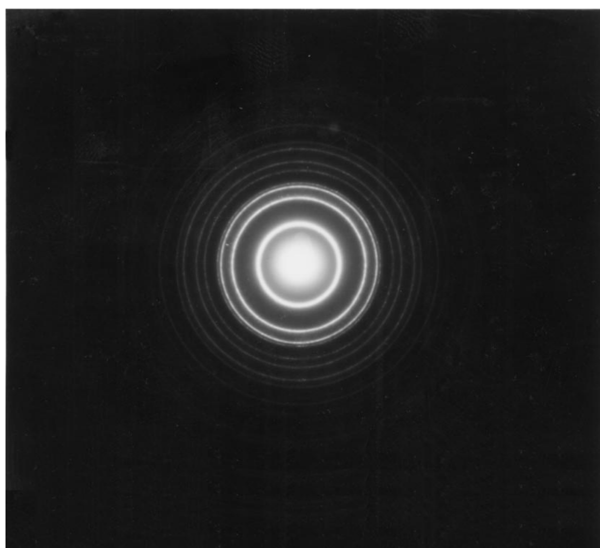
TABLE I

Sample Code	Film Thickness (nm)	Deposition Temperature (°C)	Structure of the As deposited Film	Annealing Condition after the phosphorous diffusion	Grain size (nm)	Conductivity (s/cm)	Carrier concentration (cm^{-3})	Mobility (Cm^2/v-s)
A	120	620	Microcrystalline	1000°C/2 hrs.	51.4	194.55	9.5×10^{19}	12.78
B	120	580	Amorphous	600°C/48 hrs.	28.0	476.2	1×10^{20}	26.90
C	120	580	Amorphous	600°C/48 hrs. followed by 1000°C/2 hrs.	95.5	653.6	1.3×10^{20}	30.10
D	318	620	Microcrystalline	1000°C/2 hrs.	43.3	59.5	2.5×10^{19}	15.1
E	318	580	Amorphous	600°C/48 hrs.	25.0	234.7	9.05×10^{19}	20.79
F	318	580	Amorphous	600°C/48 hrs. followed by 1000°C/2 hrs.	73.4	253.8	6.0×10^{19}	26.46

that the grain growth will be an exponential function of temperature but a linear function of time. It is also interesting to note that both 620 and 580°C deposited films experienced an exposure to 1000°C for 2 hrs, but the final grain size difference is quite significant. This can be explained in the following manner. The 620°C as-deposited sample is microrystalline to start with where no further nucleation is required, and only grain growth occurs during the heat treament. Each of these microcrystallites grows at the expense of other(s). Since a large number of grains are growing, they can only grow to a certain extent. Whereas only few microcrystallites are growing at the expense of the amorphous regions when the 580°C deposited thin films are subjected to the 600°C heat treatment. This films has a lot less number of growing crystalline grains. Thus, these crystalline grains can grow to a large extent before experiencing an advancing neighbouring grain. This results in the relatively large grain size. Similar behaviour can be observed in the case of 318 nm thick films (samples D, E and F in Table I). A typical microstructure of sample D and corresponding diffraction pattern are shown in Fig. 2.



(a)



(b)

Figure 2 (a) Dark-field transmission electron micrograph of the phosphorous doped polysilicon thin film (of 318 nm thickness and deposited at a temperature of 620°C) heat treated at 1000°C for 2 hours. (b) The corresponding diffraction pattern with sharp rings suggesting a microcrystalline structure.

It is interesting to note from Table I that the mobility of sample B is considerably higher than that of sample A in spite of the fact that the grain size in sample B is smaller than in sample A (similar behaviour is seen between the thicker samples D and E). Further, when the film B is heat treated at 1000C for two hours as in A even though the grain size grows considerably (see sample C in the Table), the mobility improves only slightly. This can be explained in terms of texture or preferential grain growth of thin films. Generally these as-deposited microcrystalline films develop a texture, whereas a random orientation is observed among the crystallites forming out of the heat treated amorphous films, as suggested by the TEM study. Thus, no strong texture is observed in the case of heat treated amorphous samples (B & C). Absence of texture results in higher mobility compared to the case where texture is present. Similar behaviour could be observed in the case of 318 nm thick film. The carrier concentrations are averaged over the entire film.

In a thicker film the average doping is lower than that in a thinner film. Therefore, the self diffusivity of silicon atoms is smaller in the thicker film than that observed in the thinner film [14]. Thus, the grain size and hence the mobility in thicker films are consistently small compared to those in thinner films, as observed in this study. This result indeed supports that the self diffusivity of silicon is responsible for the grain growth mechanism.

4. Conclusions

Deposition temperature and annealing condition have pronounced effects on the structure and electrical properties of LPCVD silicon thin films. If the deposition pressure is kept constant, the diffusion of silicon in the film is governed by the deposition temperature. Diffusion rate is the exponential function of temperature but the linear function of time. Higher is the rate of diffusion easier for the atoms to rearrange themselves in the film giving rise to a crystalline structure. Amorphous to crystalline transition of the growing film takes place at a deposition temperature some where between 580 and 620°C temperatures.

As-deposited amorphous film does not have a large number of nuclei which have a crystalline structure. Thus they develop large grain size when subjected to the 1000°C annealing treatment. Whereas each crystallite of an as-deposited polycrystalline film can participate in the grain growth during 1000°C annealing treatment resulting a fine grain size.

As-deposited microcrystalline film generally shows preferred orientation whereas no preferred orientation is seen in the annealed "amorphous" film. Absence of preferred orientation or texture is presumably responsible for increased mobility of these phosphorous doped films which had an amorphous structure in the as-deposited state.

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