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SHORT COMMUNICATION

THE CRYSTALLINE QUALITY OF Si FILMS PREPARED BY THERMAL- AND PHOTO-CVD AT LOW TEMPERATURES

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Abstract—Various silicon films were prepared by thermal- and UV photo-CVD processes. The reactants were SiH_4, Si_2H_6, SiH_2F_2, SiF_4, and H_2. Silicon films grown at temperatures below 500℃ were either amorphous or crystalline depending on the process conditions, and the growth rates ranged between 5 and 80 Å/min. The film obtained by photo-CVD using fluoro-silanes as the reactants was crystalline even when the deposition temperature was as low as 250℃. Analyses of the film by RBS, SIMS, XRD, and *ex-situ* IR indicated that the film grown from silanes was contaminated by oxygen and other impurities while one from fluoro-silanes was relatively low in the impurities. The film crystallinity was higher in the latter case than the former.

Key words: *Crystallinity, Si-Film, Photo-CVD, Fluorosilane*

INTRODUCTION

Low-temperature growth of device-quality thin silicon films has become very important, in particular for the purpose of fabricating submicron electronic devices. Recently, thin film transistors (TFTs) have been used in many fields such as liquid crystal display (LCD), image sensor and LSI application. Request for the low-temperature process comes from that ordinary glass substrates, for example in the case of TFTs, cannot endure high-temperature processing, and the modern submicron IC devices have the problems of autodoping and solid-state out-diffusion at high temperatures.

Several methods have been proposed for this purpose, such as molecular beam epitaxy [Ota, 1979], low-pressure chemical vapor deposition [Meyerson, 1986], and plasma enhanced chemical vapor deposition [Donahue and Reif, 1985].

This paper reports the results of thermal- and photo-CVD to obtain both amorphous and crystalline silicon films under various process conditions. SiH_2F_2 and SiF_4 were used as the reactants, and the role of fluorine in the system was studied. The films were examined by Raman, FT-IR, RBS, and XRD methods.

EXPERIMENTAL METHODS

A typical cold-wall/hot-susceptor CVD reactor made of stainless steel was connected to an UHV chamber for analysis of the reaction mixture with quadrapole mass spectrometer. The reactor accommodated wafers of diameter up to 4 inches.

Various silicon films were prepared by two different methods of deposition. One was a conventional thermal-CVD, and the other a photo-CVD. Mercury was used as a UV-sensitizer in photo-CVD to complement the low extent of optical absorption in the 190-200 nm wavelength region by the reactant molecules [Nishida et al., 1984; Hamasaki et al., 1984]. A low-pressure mercury lamp (manufactured by Kumkang, Co.) was employed as a light source. A synthetic quartz (Suprasil) window, transparent to the 185 nm line, was placed between the lamp and substrate, with its surface exposed to the reactants coated with a high-vacuum grease (APIEZON L-type). SiH_4, Si_2H_6, SiH_2F_2, SiF_4, and H_2 were used as the reactants. The substrate was a boron-doped, (100)-oriented silicon wafer and the surface was cleaned *ex situ* by dipping in an aqueous solution of 10 mol% HF for 1 min followed by immediate purging with dry hydrogen. Amorphous and crystalline silicon films were grown at temperatures below 500℃ to the thickness ranging from 1000 to 5000 Å.

Raman spectra of the films were obtained in the near-backscattering geometry using an Ar^+ ion laser at 5145 Å and a double SPEX monochromator in the spectral range of 400-700 cm^{-1}. The exciting laser power was kept below 400 mW to avoid annealing of the samples by the laser power. All the spectra were measured at the resolution of 0.2 cm^{-1}.

The IR spectrophotometer used was a MIDAC high resolution FT-IR with the spectral range of 400-4500 cm^{-1}. Spectra were accumulated with 100 scans, at the resolution of 4 cm^{-1}. In all the absorbance measurements, bare silicon substrate was used as a reference.

RBS (Rutherford Backscattering Spectra) were measured in random or 165°channeled geometry. The source of RBS was 2.236 MeV $4He^{++}$ (3SDH, NEC). Crystalline quality of the film was also evaluated by XRD (D/MAX II-A, Rigaku).

RESULTS AND DISCUSSION

1. Analysis of Raman Spectra

Fig. 1 illustrates typical Raman spectra of the sample films grown by thermal- and photo-CVD. The spectra are resolved into two major peaks in the range between 450 and 560 cm^{-1}, *i.e.*, a sharp peak at 521 cm^{-1} assigned to crystalline silicon and a broad one at 480 cm^{-1} due to amorphous silicon [Shibada et al., 1987; Marvilie and Reif, 1992]. By comparing the relative intensities of the two peaks, we may estimate the crystallinity of the sample films. The results show that photo-CVD produces a more

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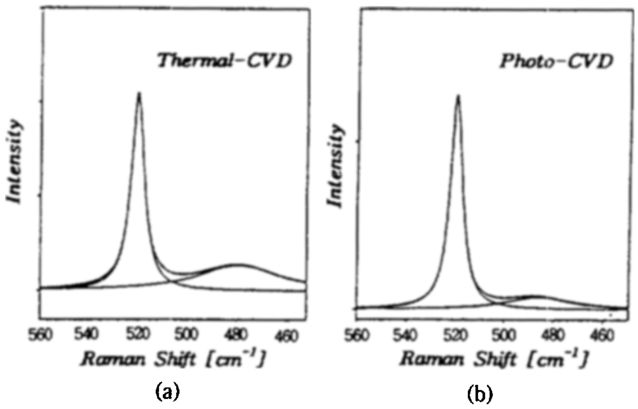

Fig. 1. The deconvoluted Raman spectra of (a) thermal-CVD and (b) photo-CVD with the conditions of $Si_2H_6/SiH_2F_2/H_2=1/25/125$, 2Torr, 250°C, and 4.5 hr.

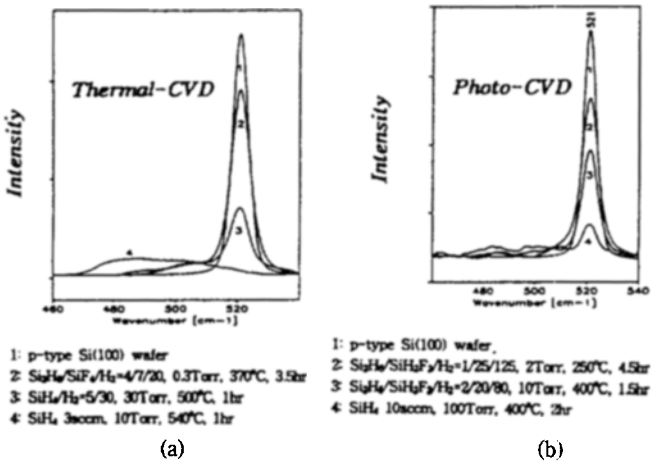

Fig. 2. The Raman spectra of the silicon films prepared at various conditions by (a) thermal-CVD and (b) photo-CVD.

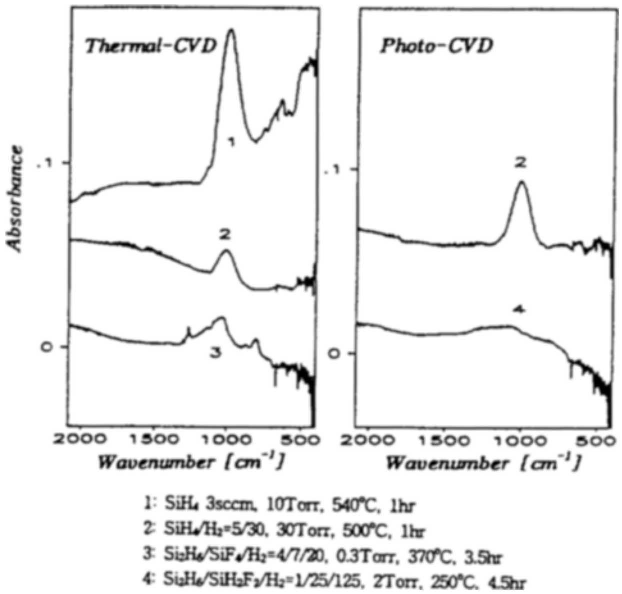

Fig. 3. FTIR absorbance spectra of the Si films prepared with the various reactant mixtures.

crystalline film than thermal-CVD. Similar analyses of Fig. 2 indicate that the crystallinity was improved when hydrogen or fluorosilanes were added to the reactant stream. It is noticeable that a crystalline film is obtained even below 400°C when the feed contains fluoro-silanes.

Matsuda [1983] has indicated that hydrogen radicals, when they exist in proper amounts on the silicon substrate, reduce the energy barrier for surface migration of the silicon precursors. He has also proposed that fluorine radicals replace some amounts of hydrogen on the surface thus modifying the population of hydrogen on the film.

Besides control of the hydrogen population, the surface fluorine plays another role in growth of a silicon film. That is, fluorine radicals protect the silicon surface from oxidation, maintaining the surface free of crystalline defects. This is supported by our FTIR observation described in the next section.

2. Infrared Spectra

Fig. 3 shows the IR spectra of films obtained under various CVD conditions. The major peak observed near 1000 cm^{-1} may be assigned to either the Si-F stretching, the Si-H bending or the Si-O stretching mode [Brodsky et al., 1977; Masson et al., 1984; Shimada et al., 1980; Falcony et al., 1991], but the Si-O stretching mode seems to be a correct one for the following reasons.

The peak is not due to the Si-F stretching because it is observed even in the case of SiH_4-CVD, which is devoid of the Si-F bond. The Si-H bond on the samples is negligible because no spectra show a band at 2000-2100 cm^{-1} corresponding to the Si-H stretching mode.

Except for the case of photo-CVD using SiH_2F_2, all the samples show a band near 1000 cm^{-1} indicating that the films have been oxidized to some extents during the CVD process. In fact, it has been reported [Yabumoto et al., 1990] that silicon suboxides ($SiO_{0.5\text{-}0.7}$) grow on the surface at temperatures above 500°C even when the partial pressures of O_2 and H_2O are as low as 4×10^{-9} Torr and 3×10^{-9} Torr although the surface has been pre-cleaned by an HF solution. This is because the surface hydrogen groups introduced during the pre-cleaning step, which are necessary to protect the surface from oxidation, desorb at elevated temperatures.

In Fig. 3, the Si-O peak is relatively small in the case of thermal-CVD with SiF_4 and is not even observed on a film obtained by photo-CVD with SiH_2F_2. A common factor in these two cases is that they have used fluoro-silanes as reactants. Thus, fluorine suppresses oxidation of the silicon surface.

These IR results together with the above Raman results suggest the following two roles of fluorine in the CVD process. One is to modify the hydrogen population on the surface and the other is to protect the silicon surface from oxidation.

3. RBS, SIMS, and XRD Analyses

The CVD films obtained in this study have been analyzed further for their thickness, crystallinity and possible impurities. Fig. 4 shows RBS spectra of a film obtained by thermal-CVD with SiH_4 and H_2 at 500°C. The spectra have been probed by 2.236 MeV He ions. The channelled spectrum shows an obvious contrast to the random one, and indicates that a layer of 350 Å thickness has been deposited on the substrate whose surface is distinguished by signals of defects and contaminants. The channelling yield (χ_{min}) is about 13%, slightly higher than for the bulk silicon.

The negative SIMS profile of a 1.75 μm-thick film obtained

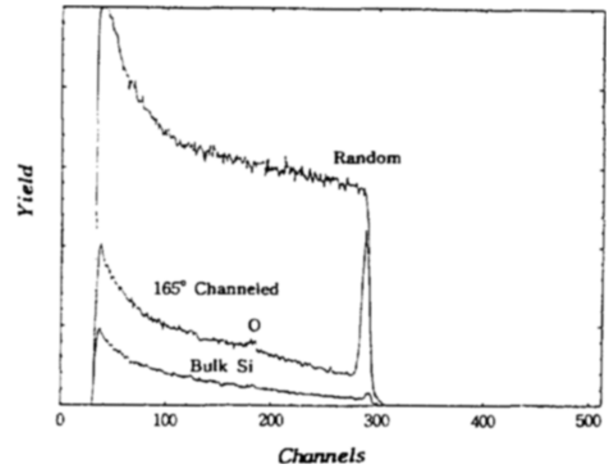

Fig. 4. RBS random and channeling spectra probed by 2.236 MeV He^{++}. The film prepared with the conditions of $SiH_4/H_2=5/30$, 30 Torr, 500°C, and 1 hr.

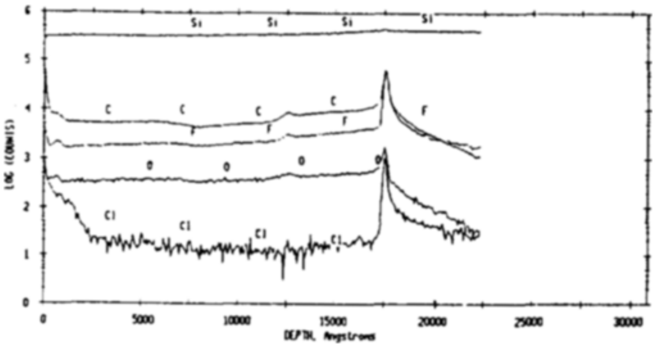

Fig. 5. Negative SIMS profile of the low-crystalline Si film obtained by thermal-CVD with Si_2H_6, SiF_4, and H_2 at 370°C.

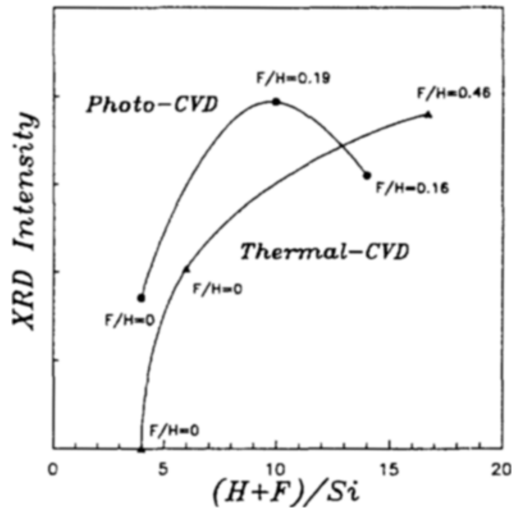

Fig. 6. XRD peak-intensity plot of the prepared crystalline silicon films. (H+F)/Si and F/H are the ratios of each atom in the reactants.

by thermal-CVD with Si_2H_6, SiF_4, and H_2 at 370℃ (Fig. 5) also shows the suboxides ($SiO_{0.5\text{-}0.7}$) and the carbon and fluorine contaminants at the film-substrate interface. Thus, the results indicate that, although our CVD experiments have been made with many contaminations, the films obtained by photo-CVD with fluoro-silanes are highly crystalline as analyzed by Raman spectra.

Crystallinity of the films, as estimated from the XRD-peak intensity, varies with the process conditions as shown in Fig. 6. The following general trends may be derived from the results: photo-CVD yields higher crystallinity than thermal-CVD. The crystallinity improves when the amount of hydrogen and fluorine increases in the feed. In the case of photo-CVD, an optimum (H+F)/Si ratio in the reactants exists that yields a film of the highest crystallinity.

CONCLUSION

Silicon films have been grown by thermal- and photo-CVD with or without fluoro-silanes in the feed at 250-500℃. The films have been characterized by Raman, RBS, XRD, SIMS, and *ex-situ* FTIR.

The results indicate that the silicon-film crystallinity is improved by photo-CVD and by addition of fluoro-silanes in the feed at temperatures as low as 250℃.

Fluorine on the silicon surface plays two roles in the film growth. One is to modify the hydrogen population on the surface and the other is to protect the silicon surface from oxidation.

Except for the case of photo-CVD using SiH_2F_2, all samples contained some undesired suboxide silicon in the deposited film. This oxide deteriorated the film crystallinity at low temperatures.

When SiH_2F_2 was used in the feed, highly crystalline silicon film was obtained at 250℃ with no suboxide in the film.

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