The Thin Silicon Films Prepared by Thermal- and Photo-CVD at Low Temperatures

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I. Introduction

Low-temperature silicon growth of device-quality thin 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. Particularly, crystalline films have been vigorously investigated because of its superior electrical characteristics. However, since ordinary glass substrates cannot endure high-temperature processing in case of TFTs and submicron devices have the many problems of autodoping, solid-state out-diffusion, . . . at high temperature, it is necessary to develop low temperature crystalline-silicon growth methods.

This letter reports the results of both amorphous film and crystalline silicon film by thermal- and photo-CVD under variable conditions of gas mixtures. The films have been studies with the optical techniques of Raman spectroscopy, as well as with FT-IR measurement. RBS and XRD were also performed.

II. Experimental Details

A variety of silicon films were prepared in each of two different methods of deposition. One of these methods was a conventional thermal-CVD , and the other was photochemical vapor deposition process. The mercury photo-sensitization method was used in photo-CVD to enhance the dissociation of reactant gases beause of the small amount of optical absorption by the molecules in the 190-200nm wavelength region[1,2]. A low-pressure mercury lamp was employed as a light source. A synthesis quartz-glass (suprasil) window, which transmits a 185nm resonance line, was coated with a low-vapor-pressure vacuum grease (APIEZON L-type), and was placed between the lamp and substrate. As the reactants, SiH_4, Si_2H_6, SiH_2F_2, SiF_4 and H_2 were used.

Films were prepared on boron doped (100)-oriented silicon wafer. Amorphous and crystalline silicon films were grown at low temperatures below 540℃ with a thickness ranging from 1000 to 5000Å.

The Raman measurements were performed in the near-backscattering geometry using an Ar^+ ion laser at 5145Å and a double SPEX monochromator in the spectral range 400-700cm^{-1}. All spectra were measured with the the resolution of 0.2cm^{-1}.

The IR spectrophotometer used was a MIDAC high resolution FT-IR in the range of 400-4500cm^{-1}. Spectra were accumulated with 400 scans, at a resolution of 4cm^{-1}. All the absorbance measurements were made relative to an uncoated reference silicon substrate.

III. Results and Discussion

A. Analysis of Raman Spectra

Figure 1 illustrates typical Raman spectra for single crystalline silicon (reference silicon wafer) and processed amorphous silicon films. A sharp peak at $521cm^{-1}$ (TO) attributed to crystalline silicon is observed, whereas the broad peak at $480cm^{-1}$ (TO) related to amorphous silicon[3].

Figure 2 shows the deconvoluted Raman spectra of the samples as grown by thermal-CVD and photo-CVD, respectively. In addition to the peak at $521cm^{-1}$, there is a shoulder at about $500cm^{-1}$ in curves. The shoulder indicate that the deposited films have disordered phase in some magnitude[4].

We found that the crystallinity improved with the addition of hydrogen. Furthermore, addition of fluorine contained chemicals improved the film crystallinity whereas the temperature was drastically reduced. It might be that the hydrogen radicals reduce the barrier height associated with the surface migration of the precusors by covering the growing surface[5], and that the fluorine radicals introduced by the addition of SiH_2F_2 or SiF_4 serve to extract the exess bonded hydrogen on the growing surface in the low temperature process.

In addition, we suggests that fluorine radicals might play another important role in crystalline silicon film growth. It is that fluorine radicals prevent silicon surface from attacking of gas phase oxygen and remove surface oxygen. This fact was examined with FT-IR investigation discussed in section III B.

B. Infrared Properties

It is difficult to assign the corresponding IR absorption, since the Si-F bond stretching vibrations appear in the same frequency regions as the Si-H bond bending and the Si-O bond stretching vibrations. Fortunately, the typical IR spectrum of Si-H has absorption band at $1900\text{-}2100cm^{-1}$ assigned to stretching mode. Therefore, if there is no absorption band at about $2000cm^{-1}$, the absorption band near at $1000cm^{-1}$ is not caused by Si-H stretching mode. In this work, Si-H stretching mode appeared in the sample of thermal-CVD using only SiH_4 gas as the reactant.

Except the case of photo-CVD sample using fluorine contained chemicals, all spectra have absorption band of suboxide silicon near at $1000cm^{-1}$ as shown in figure 3. Yabumoto *et al.* reported that the oxide regrowth on the silicon surface cleaned by an HF solution (terminated by hydrogen) proceeds even in the low pressures of O_2 and H_2O (4×10^{-9}Torr and 3×10^{-9}Torr) after hydrogen desorption from the silicon surface[6]. From this fact, we consider that, in conventional silicon deposition reactant (not fluorine contained chemicals), the oxide could easily grown by the residual O_2 and H_2O in the reactor during processing at the deposition temperature (*See* RBS spectrum in figure 4).

The frequence of the peak scales monotonically with the oxygen atom concentration with values of $1075cm^{-1}$ in stichiometric SiO_2 to $950cm^{-1}$ in O doped amorphous silicon (SiO_x, $x<2$)[7]. And the broading of the band is a manifestation of a statistical distribution of different bonding arrangements at each silicon atom site. As shown in figure 3, comparatively discussion with Raman spectra, we can easily find that the addition of hydrogen and fluorine contained chemicals keep the growing surface away from residual oxygen during process.

IV. References

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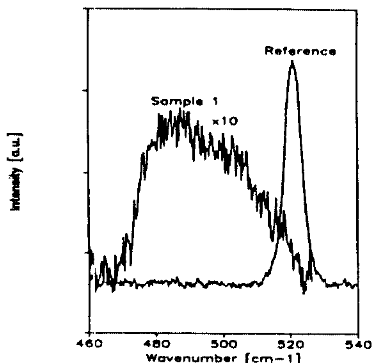


Reference: p-type Si (100) wafer

Sample 1: SIH4 3sccm, 10Torr, 540°C, 60min

Figure 1. The typical Raman spectra of amorphous and crystalline Si.

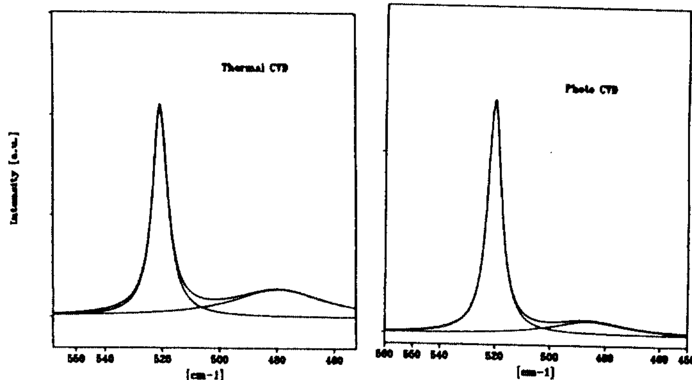
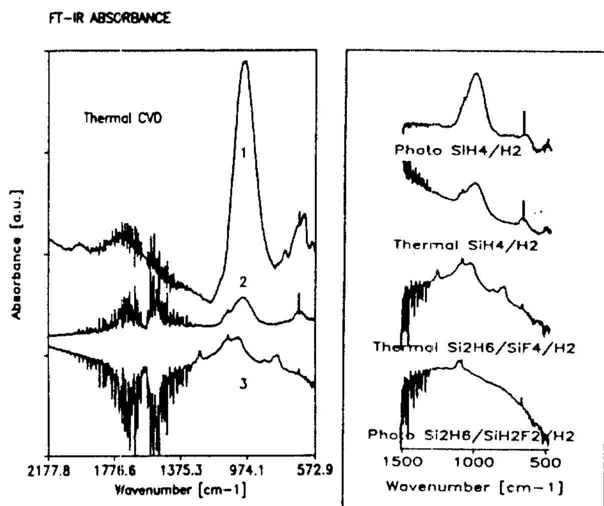


Figure 2. The deconvoluted Raman spectra of thermal-CVD and photo-CVD.



1: SiH4 3sccm, 10Torr, 540℃, 1hr

2: SiH4/H2=5/30, 30Torr, 500℃, 1hr

3: Si2H6/SiF4/H2=4/7/20, 0.3Torr, 370℃, 3.5hr

Figure 3. FT-IR absorbance spectra.

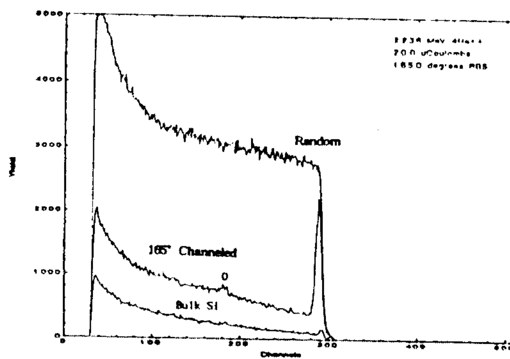


Figure 4. RBS random and channeling spectra.