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Low Temperature Formation of Polysilicon Films by Catalytic Chemical Vapor Deposition (Cat-CVD) Method

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Polysilicon films are obtained at temperatures lower than 410 °C by the catalytic chemical vapor deposition (cat-CVD) method, in which gases are decomposed by reactions with a heated catalyzer near substrates, when the gas pressure during deposition is kept below a certain critical value. Grains are preferentially oriented along the (220) direction, grain size is about 500 to 1000 A. The Hall mobility is usually about several cm^2/Vs and occasionally appears to reach an even much higher value by adjusting deposition parameters.

1. Introduction

Low temperature formation of polysilicon (poly-Si) films with high mobility is strongly required for the fabrication of thin film transistors (TFT) used in liquid crystal displays. The laser annealing of amorphous silicon (a-Si) is one of promising techniques to obtain such poly-Si films [1,2], apart from the conventional high-temperature thermal annealing of a-Si. However, since only small areas can be poly-crystallized by the laser annealing, the development of other methods to obtain poly-Si films at low temperatures with a wide area is also strongly desired.

The author and his co-workers have developed a new low temperature deposition method, named as catalytic chemical vapor deposition (cat-CVD) method [3,4]. In the method, deposition gases are decomposed by the catalytic or pyrolytic reaction with a heated catalyzer placed near substrates, and thus, wide-area films are deposited at low temperatures without help from plasma or photochemical excitation. Actually, the author has succeeded to obtain high-quality a-Si [5], silicon-germanium [6], and also silicon-nitride films [7] at the temperatures lower than 300 °C by this cat-CVD method.

In the way of the investigation to obtain even higher-quality a-Si, the author discovered that silicon films were easily polycrystallized at low temperatures when gas pressure during deposition Pg was kept below a certain critical value Pg_c and also when the film was thicker than a certain thickness [8]. This paper is to report the properties of this cat-CVD poly-Si film in addition to the discovery of polycrystallization itself, although the research is still too preliminary to judge the usefulness of the films as the material for TFT.

2. Fundamentals

Deposition apparatus of cat-CVD method is already reported in several papers [5-7]. The apparatus used here is almost same as that reported, apart from the pumping system. In the present system, the deposition chamber is pumped by a diffusion pump to obtain films under wider range of Pg.

A tungsten wire of a diameter of 0.35 mm is used as the catalyzer and placed at just beneath substrates by a distance of 4 cm. A total surface area of the wire is about 16 cm^2. The temperature of catalyzer T_{cat} is kept at 1300 to 1390 °C, and an amount of electric power supply to the catalyzer PW_{cat} from 300 to 1000 W. A SiH_4 and H_2 gas mixture is used as the deposition gases, and a flow rate of SiH_4, FR(SiH_4), is kept at about 20 sccm and that of H_2, FR(H_2), at about 40 sccm. The temperature of substrate holder T_{sh} is measured by a thermocouple T.C. placed just besids the substrates, and the substrate temperature itself T_{ss} is measured by painting "Thermo-Paints" on the back side of the substrates. The "Thermo-paint" is a special paint whose colour changes irreversibly at a particular temperature.

3. Poly-Si Formation and Its Properties

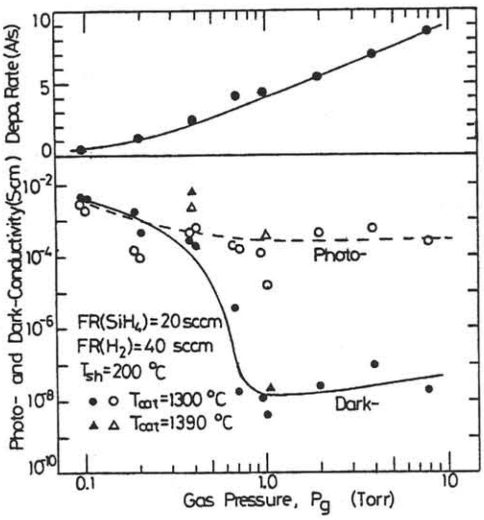

Fig.1 Deposition rate, photo- and dark-conductivity vs Pg.

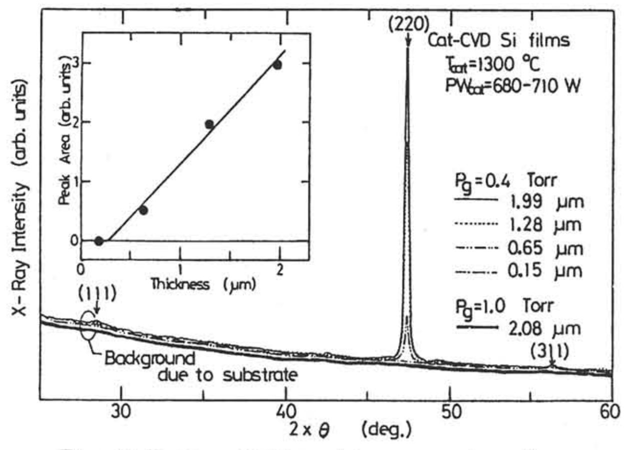

Fig.2 X-ray diffraction spectra for samples of Pg=0.4 Torr and 1 Torr.

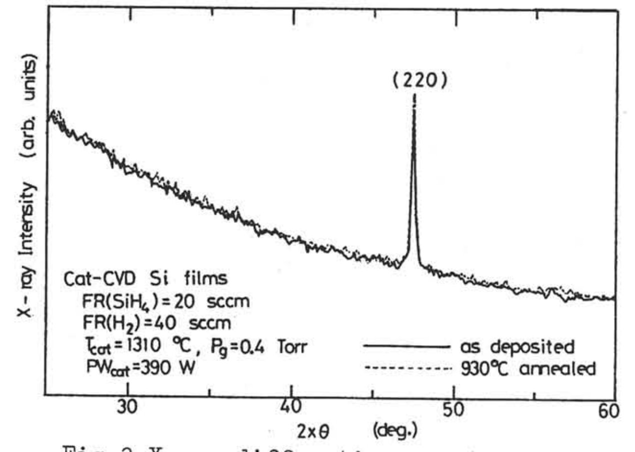

Fig.3 X-ray diffraction spectra to know volume fraction of poly-silicon phase.

In the investigation to obtain even higher-quality a-Si by the cat-CVD method, silicon films were deposited under the various gas pressures, and the photo-conductive properties were measured for such films as shown in Fig.1. In the figure, the deposition rate, the photo-conductivity under the illumination of AM-1 of 100 mW/cm^2 and the dark-conductivity are plotted as a function of Pg. Since it was known from the results that the film produced at Pg below about 0.7 Torr was apparently different from that at Pg over 0.7 Torr, next, the structure of the low-Pg films was observed by a X-ray diffraction spectroscopy.

Figure 2 demonstrates the X-ray diffraction spectra for silicon films deposited at Pg=0.4 Torr, by taking the thickness of films as a parameter. It is clearly found that the films are polycrystallized when the thickness exceeds a certain value, and that the grains of such poly-Si films are likely to be oriented only along the (220) direction. In the inset of the figure, the areas of diffraction peaks are plotted versus thickness. From this inset, it is estimated that the certain critical thickness is about 0.2 to 0.3 micron-meters. Since it is confirmed that the films of high-Pg are amorphous by the same X-ray diffraction experiments, it is concluded that the change of the photo-conductive properties shown in Fig.1 is attributed to the polycrystallization.

Figure 3 demonstrates a similar X-ray diffraction spectrum of the film of thickness of about 0.7 micron-meters along with another spectrum of the same film after annealing at 930 °C in nitrogen atmosphere. From the comparison of two diffraction peaks, the volume fraction of poly-Si is known as about 90 %.

In order to know the mechnism of poly-crystallization, first, T_{ss} was monitored and compared with T_{sh}. Figure 4 shows the result. Even if T_{sh} is kept constant, T_{ss} is likely to elevate when Pg lowers. The result is quite understandable, because the ability of gas-cooling of the growing surface should be weakened for low Pg, and the influence of heat-radiation from the catalyzer becomes dominant. Thus, next, the similar experiments were again carried out for almost constant T_{ss}. To keep T_{ss} constant, T_{sh} was adjusted for the various Pg's.

Figure 5 shows the grain size estimated from the X-ray diffraction spectra, T_{ss} and T_{sh} as a function of Pg. It is known from the figure that the films are polycrystallized for Pg lower than about 0.7 Torr, even if T_{ss} is kept almost constant or slightly increases for high-Pg region. The fact shown in the figure implies that the polycrystallization does not occur due to only the heating of the substrate. Even if the substrate is heated, the film becomes amorphous for high Pg. Probably, the surface reaction of the growing film, which is balanced in between the heat-radiation from the catalyzer and the gas-

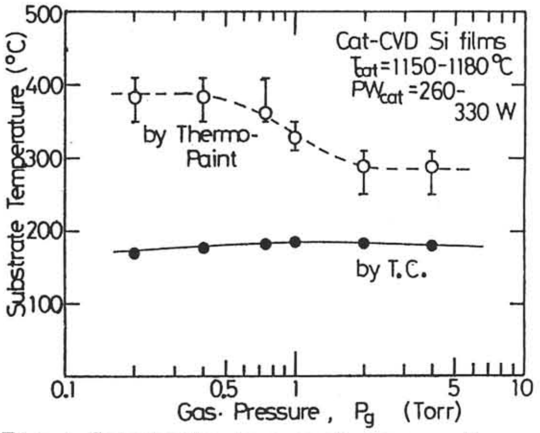

Fig.4 Substrate temperatures vs Pg. Open and closed circles refer to T_{ss} and T_{sh}, respectively.

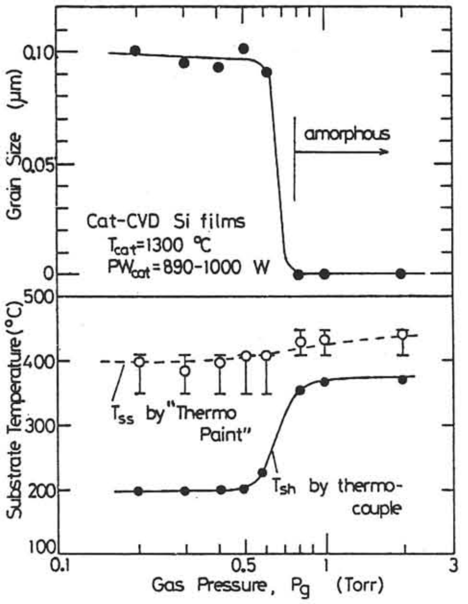

Fig.5 Grain size and substrate temperatures vs Pg.

Table I Properties of cat-CVD poly-Si.

Deposition conditions				Properties	
Pg	T_{cat}	T_{sh}	T_{ss}	Resistivity	Hall mobility
0.4 Torr	1300 °C	200 °C	<410 °C	10^1–10^2 ohm-cm	2 - 8 cm^2/Vs
0.4 Torr	1300 °C	300–360 °C	——	10^3–10^6 ohm-cm	40 - 120 cm^2/Vs

cooling, may play a key role in determining the film structure.

The electrical properties of the poly-Si were also measured mainly by the Van der Pauw method. The poly-Si films in Fig.5 show relatively low resistivity, around 10^1 to 10^2 ohm-cm, and in such a case, the measurement of Hall mobility is easy but the measured values are not so high, around 2 to 8 cm^2/Vs. When T_{sh} is incresed from 200 °C to 360 °C, occasionally films of the resistivity as high as 10^3 to 10^6 ohm-cm are obtained. For such films, the Hall-mobility measurement does not appear easy, due to the noise probably coming from an electric magnet. Although the measurement is preliminary for such films, the Hall mobility sometimes appears to reach about 100 cm^2/Vs. The properties of cat-CVD poly-Si films are summarized in Table I.

4. Conclusions

From the above studies, the follows are concluded;

1) Poly-Si films can be obtained by the cat-CVD method at the temperatures T_{ss} less than 410 °C, when Pg is lower than a certain critical value Pg_c. The Pg_c appears about 0.7 Torr under the present conditions.
2) The grains of the cat-CVD poly-Si films are likely to be oriented along only the (220) direction, and the grain size is 500 to 1000 A usually. (Here, only the results of grain size of about 1000 A are demonstrated.)
3) The Hall mobility of the cat-CVD poly-Si films whose properties can be measured without particular difficulty is usually 2 to 8 cm^2/Vs, but by changing the deposition parameter such as T_{sh}, it sometimes appears to reach about 100 cm^2/Vs, although the research is in a preliminary stage at present.

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