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Doping Control in LPCVD in-situ Boron Doped Polysilicon

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In order to form boron-doped poly-Si with sufficiently low resistivity, low-pressure CVD of in-situ boron-doped silicon films has been investigated with the idea of first depositing amorphous Si containing high concentration of boron atoms and then annealing. A low resistivity of 1.7 mΩ·cm was attained when amorphous Si was deposited at 350°C using a Si_2H_6/B_2H_6 mixture and annealed at 600°C. In addition to this, a conformal deposition profile and uniform boron concentration was also achieved in films deposited on many wafers loaded in a batch-type reactor, by a result of the deposition being controlled by the surface reaction at the low temperature of around 350°C.

1. INTRODUCTION

In situ boron-doped poly Si is a useful material for a gate electrode and an interconnection of ULSI devices since it is compatible with low-temperature processes. However, use of conventional in-situ boron doped poly-Si[1] also entails several problems, for example, its resistivity is not sufficiently low, and there is a large distribution in boron concentration among wafers loaded in a batch-type reactor. The scatter in boron concentration is thought to be caused by limitation of the process due to transport of gas molecules onto the substrate surface.

Low-temperature annealing of doped amorphous Si film has been proposed as a method of forming phosphorous- and antimony-doped poly-Si with low resistivity.[2-3] This improves not only resistivity but also the distribution of boron concentration, if the deposition temperature is reduced to the point where deposition is not limited by mass transfer, but rather by the surface reaction.

This paper reports the deposition characteristics of amorphous Si employing Si_2H_6/B_2H_6 mixture and the effects of annealing on its electrical properties.

2. EXPERIMENTAL

The experiments were carried out using a vertical hot-wall reactor. A mixture of Si_2H_6 and B_2H_6 (10% in He) was used as the source gas with a B_2H_6/Si_2H_6 gas ratio of 2×10^{-2} since this mix gives a much greater deposition rate than SiH_4/B_2H_6, according to a preliminary experiment. A Si substrate covered with a 100 nm-thick SiO_2 film was placed in the reactor. The substrate temperature and gas pressure were 350°C and 0.1 Torr, respectively. The film thickness and boron concentration were measured using a reflectometer and SIMS, respectively. Furthermore, the resistivity and Hall mobility of the Si films were measured by Van der Pauw method.

3. RESULTS AND DISCUSSION

3.1 Deposition Characteristics

Figure 1 shows the variation in deposition rate with the substrate temperature. The deposition rate saturated at temperatures above 500°C and decreased monotonously with the reciprocal temperature below 500°C.

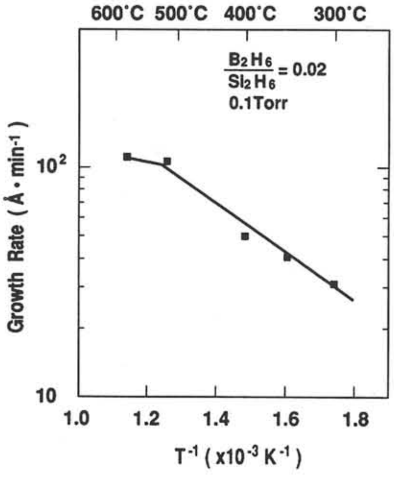

Fig. 1 Growth rate as a function of substrate temperature with the Si_2H_6/B_2H_6 mixture.

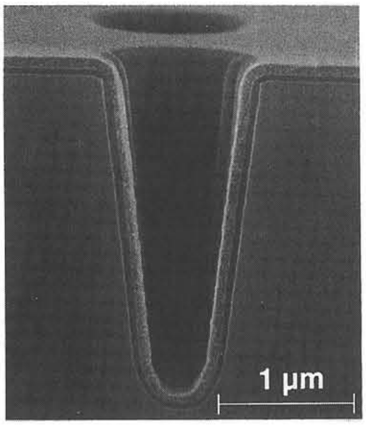

Fig. 2 SEM photograph of a trench partially filled with boron doped silicon film deposited from Si_2H_6/B_2H_6 mixture at 350°C.

Above 500°C, it can be considered that deposition is limited by the transport of gas molecules to the substrate surface, while it is controlled by the surface reaction below 500°C.

Figure 2 shows the profile deposited on a substrate fabricated with a trench 1.0 micron wide and 2.5 microns deep. Deposition was carried out at 350°C after growing thermal oxide for the purpose of decoration. If deposition is limited by mass transport, the film thickness at the trench bottom would be thinner than that at the top surface because of the shadowing effect of the trench top. However, the film has a uniform thickness from the top to the trench bottom. This indicates that the film deposition process is not *limited by mass transfer*, but is controlled instead by the surface reaction.

Next, the structure of the deposited film was analyzed using X-ray diffraction. It was found out that the film deposited at 520°C is polycrystalline with <110> preferred orientation, while the film deposited at 350°C is amorphous. Consequently 350°C is suitable for deposition of amorphous Si under surface reaction controlling conditions.

3.2 Boron Concentration

The boron concentration in the film was measured using SIMS. Figure 3 shows the variation in boron concentration as a function of deposition temperature. The boron concentration in the film was independent of deposition temperature and was much higher than the solubility limit for boron in Si even at low temperatures such as 350°C.

It was reported that the addition of B_2H_6 enhanced the decomposition of Si_2H_6 to give the high deposition rate.[4] Actually, no film was deposited using a Si_2H_6 alone at 350°C in this study. This fact suggests that B_2H_6 is not merely incorporated in the film, but reacts with Si_2H_6 molecule on the surface to enhance the decomposition of Si_2H_6. The number of boron atoms incorporated in the film is determined by the stoichiometry of this reaction. Therefore, the boron concentration is considered to be independent on

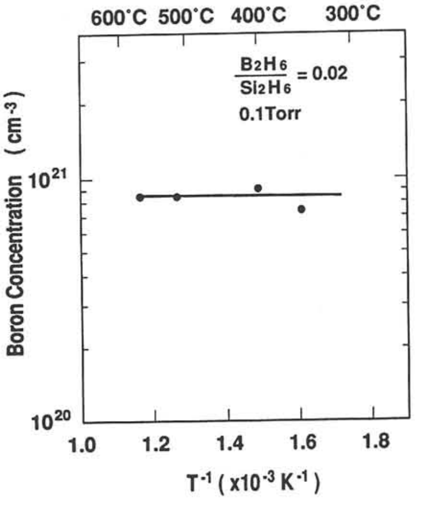

Fig. 3 The variation in boron concentration as a function of substrate temperature.

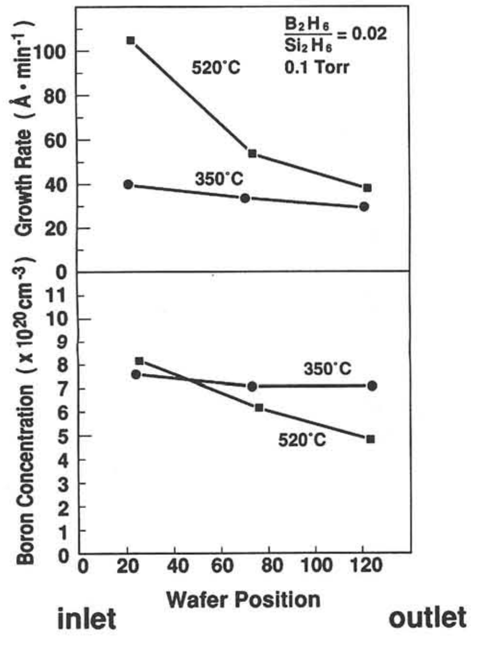

Fig. 4 The distributions in boron concentration and growth rate among wafers in a reactor at deposition temperatures of 520°C and 350°C.

the substrate temperature.

Figure 4 shows the distribution of deposition rate and boron concentration among wafers loaded in a reactor. The gas flowed from left to right in the figure. The deposition rate and boron concentration decreased between the inlet and outlet at 520°C. The amount of source gas molecules decreased with inlet to outlet because of consumption in deposition, since deposition was limited by the mass transport. On the other hand, a uniform deposition rate and boron concentration was achieved at 350°C, because the process was controlled by the surface reaction. The wafer to wafer uniformity in boron concentration over a 100-wafer load was in the ±10% range.

3.3 Effects of Annealing on Film Structure and Electrical Properties

Films deposited at 350°C were annealed at several temperatures in a N_2 ambient for 60 minutes. The change in film structure was analyzed by X-ray diffraction and plane TEM. No specific signal were observed in the X-ray diffraction spectrum of films annealed at 500°C, indicating that the film was still amorphous. However, crystallization was observed when the film was annealed at 600°C. Figure 5 is a plane TEM photograph of film. It should be surprising that the grain grew to 3 ~ 4 μm, which is 5 or 6 times larger than that of conventional boron doped poly-Si. The grain size grew slightly larger with annealing above 600°C. It can be considered that reduced generation of nucleation center in amorphous Si leads to this large grain, as previously reported.[3]

The electrical properties were measured next. Figure 6 shows how the resistivity of the film varies with annealing temperature. The resistivity of the as-deposited film was 10^2 Ω·cm. This value remained unchanged if the film was annealed below 500°C, because crystallization did not occur up to 500°C as described above. However, annealing at 600°C resulted in a drastic decrease in resistivity to 1.7 mΩ·cm, which is about 1/3 ~ 1/2 the value for conventional boron doped poly-Si. It should be noted that this low resistivity film was obtained at low temperature of 600°C. At temperatures above 600°C, the resistivity increased slightly with annealing temperature.

The carrier concentration and Hall mobility were measured using the Van der Pauw method in order to clarify the reason of low resistivity. Carrier concentration in the film annealed at 600°C was 2 x 10^{20} cm^{-3}, which was much higher than solubility limit of boron in Si in thermo-equilibrium at 600°C. This is evidence that the poly Si supersaturated with boron. On the other hand, the Hall mobility in the film annealed at 600°C was 16 $cm^2 \cdot V^{-1} \cdot s^{-1}$, which was twice larger than that of the conventional boron doped poly-Si films. It is considered that the film consisted of the large grain brings about this higher mobility. Consequently low resistivity is realized by both the high carrier concentration and higher mobility.

Fig. 5 TEM photograph showing the grain structure of boron-doped polysilicon annealed at 600°C for 60 minutes.

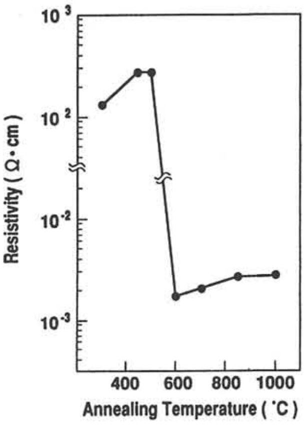

Fig. 6 Resistivity as a function of annealing temperature, this film was deposited using Si_2H_6/B_2H_6 at 350°C.

SUMMARY

The formation of in-situ boron-doped poly-Si has been studied using in two stages consisting of amorphous Si deposition and subsequent annealing. The annealing of the amorphous Si containing boron atoms at above the solubility limit increases the grain size 5 or 6 times, leading to a sufficiently low resistivity of 1.7 mΩ·cm. In addition, a uniform boron concentration was achieved, since the deposition process was controlled by the surface reaction at 350°C.

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