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Thin Solid Films 379 (2000) 213–217

thin solid films

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Plasma effects of fluorine implantation on As^+-doped polycrystalline silicon thin films of various thicknesses

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Accepted 20 June 2000

Abstract

This work studied plasma effects on the resistivity, effective free carrier concentration, and mobility of As^+-doped, F-implanted polycrystalline silicon (polysilicon) thin films of various thicknesses. It was found that the resistivity of the polysilicon thin film increases with the decrease of the thickness of the film. This is mainly due to the decrease of the effective carrier concentration and mobility through the decrease of the grain size which is limited by the thickness of the film. Hydrogen and NH_3 plasma treatments decrease the effective carrier concentration of the film through neutralization of As ions. This effect is more evident for the thinner films (< 60 nm). The mobility of the high F-dose sample (3×10^{15} cm^{-2}) is larger than that of the low F-dose samples (1×10^{15} cm^{-2}), because the implanted F atoms passivate trapping states of the polysilicon thin film. Through the use of the F implantation passivation and the NH_3-plasma treatment, a polysilicon film of a high mobility can be obtained. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Amorphorization; Polysilicon; Neutralization; Passivation;

1. Introduction

Polysilicon is widely used in integrated circuits as interconnection lines, gate electrodes, polysilicon resistors, and device active layers for thin film transistors (TFT). It is used in the form of thin films. In order to obtain desirable characteristics of polysilicon TFTs, many techniques have been employed to improve the device performance by reducing the trap-state density or by increasing the grain size of the polysilicon film. For instance, hydrogenation is used to improve the TFT performance [1–3] since hydrogen atoms incorporated in grain boundaries of the polysilicon thin film passivate dangling bonds and release strained bonds to decrease trapped states [4]. However, it is difficult to control the hydrogen concentration in the polysilicon TFT, since weak Si–H bonds are dissociated by the stress and positive fixed charges are created. This results in a negative V_{th} shift and the degradation of the subthreshold slope of the drain current [5].

Recently, it was reported that fluorine implantation improves the characteristics of the TFT [5–8]. The implanted fluorine atoms passivate the channel polysilicon layer, for which the Si–F bonds are more stable than Si–H bonds against the bias and temperature stress. The passivating fluorine atoms increase the carrier mobility and also suppress the leakage current. Moreover, it was reported that polysilicon TFTs of an active layer of a thickness less than 50 nm exhibit a better performance than those of TFTs with thicker active layers (> 100 nm) after hydrogenation [3]. Thus, it seems that hydrogen passivates more effectively and increases the mobility for the thinner polysilicon film. Furthermore, earlier literature reported that hydrogen

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0040-6090/00/$ - see front matter © 2000 Published by Elsevier Science B.V. All rights reserved.
PII: S0040-6090(00)01188-3

neutralization on n- (or p-type) single crystal silicon creates hydrogen-donors (or acceptors) in the crystal [9–11]. This could decrease the effective carrier concentrations of the crystal Si and polysilicon film [12–14] and reduce the leakage currents in p–n junctions [15–17] when it is applied to devices.

This paper studied, in a systematic way, the fluorine implantation and hydrogen or NH_3-plasma effects on polysilicon thin films of various thicknesses. The polysilicon thin films were doped (implanted) with As^+ concentrations of 1×10^{20} cm^{-3}. The resistivity, free carrier concentration, and mobility of the films, before and after they were plasma-treated, were measured by using the resistor test structure and the van der Pauw test structure [18]. Transmission electron microscopy (TEM) was used to examine grain sizes and structures of films to help to explain the results. It is believed that the results obtained provide an understanding on the fluorine-passivation and hydrogenation mechanism for the polysilicon thin film and how they improve characteristics of TFTs.

2. Experimental procedures

Since the investigation was to help understand the fluorine passivation with plasma treatment on polysilicon TFTs, the procedure to prepare the polysilicon films in this work was the same as that used to prepare polysilicon TFTs. Firstly, a 500-nm silicon dioxide layer was grown on p-type 1–5 Ω-cm ⟨100⟩ wafers. Then undoped amorphous silicon films of 42–100 nm thicknesses were deposited in a low-pressure chemical vapor deposition (LPCVD) reactor by pyrolysis of silane at 550°C under a pressure of 100 mtorr. Following this, a pad SiO_2 of 20 nm was thermally grown on the undoped polysilicon films at 850°C in an H_2/O_2 atmosphere. Next, the polysilicon layers were implanted with As^+, giving a dopant concentration of approximately 1×10^{20} cm^{-3}. The implanted dosages and energies were chosen to make the doping concentrations of the polysilicon films of different thicknesses the same, and they are shown in Table 1 [12,14]. Some of the samples were implanted with fluorine ions with dosages of 1×10^{15} and 3×10^{15} cm^{-2} at 30 keV, respectively. After implantation, all the samples were annealed at 850°C for 60 min in a nitrogen atmosphere. Some of the samples were treated with the hydrogen plasma for 60 min, or NH_3-plasma for 60 min, respectively, in a commercial 13.5-MHz paralleled-plate plasma reactor at 300°C. The hydrogen and nitrogen gas flow rates were 60 and 60 sccm, respectively, the RF power was 200 W, and the total pressure was 100 mtorr. The test resistor bars with various lengths and widths and Van der Pauw patterns were defined photo-lithographically. Al (with 1% Si) was deposited and sintered at 300°C for 40 min in N_2 gas to form contacts on the resistor bars. Hall mobilities and effective free concentrations were measured on the Van der Pauw patterns [18], and resistor I–V characteristics were measured by an HP 4145B semiconductor parameter analyzer over a voltage range from −10 to 10 V. TEM was used to measure grain size and estimate the crystalline structure of polysilicon film to help to explain the results.

3. Results and discussion

3.1. Resistivity of polysilicon thin films

The measured resistivities vs. the film thickness before and after the hydrogen plasma or NH_3 plasma treatments are shown in Fig. 1. Each data point represents the average value of at least 10 samples. On this figure, several facts can be observed: (1) resistivities of all samples increased with the decrease of the thickness of polysilicon films; (2) they all increased after the plasma treatments; (3) the increase of the resistivity for the NH_3 plasma treatment was larger than that for the hydrogen plasma treatment; (4) the resistivity increase was larger for the samples of thinner thicknesses; (5) the resistivity of the fluorine-implanted sample was lower than that of the non-fluorinated sample; and (6) the resistivity of the sample of the lower fluorine-dose (1×10^{15} cm^{-2}) was higher than that of the sample of the higher fluorine dose (3×10^{15} cm^{-2}). In the above observations, fact (1) can be easily visualized since as the thickness of polysilicon film decreased, the surface effect became more evident, which decreased the mobility of the film. The result of fact (2) is contrary to the conventional conception, i.e. after fluorine implantation and plasma treatments, the resistivity should decrease since the mobility was improved due to passi-

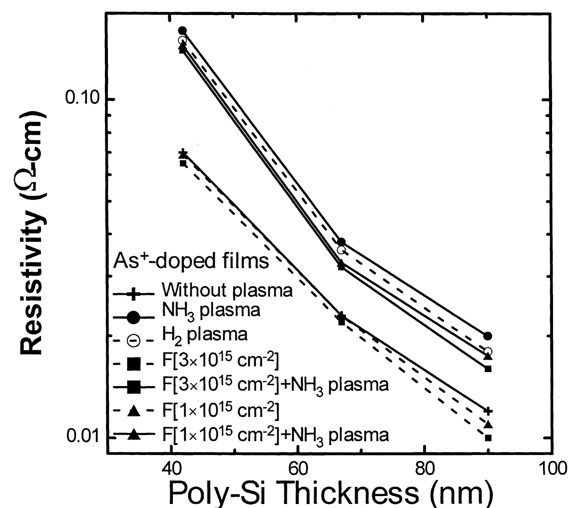

Fig. 1. The measured resistivities of plasma-hydrogenated, or NH_3-treated and/or fluorine-implanted poly-Si film vs. the film thickness, respectively.

Table 1
The different energies, dosage and calculated concentrations under various thickness

Film thickness (nm)	Dopant	Dose (cm^{-2})	Energy (keV)	Calculated concentration ($\times 10^{20}$ cm^{-3})
90	As^+	9.0×10^{14}	120	1
67	As^+	6.7×10^{14}	109	1
42	As^+	4.3×10^{14}	83	1
25	As^+	2.5×10^{14}	50	1

vation of grain boundaries of the polysilicon film. This is explained in section B with the data of Fig. 2, where the effective concentration, which is also a factor to determine the resistivity of the polysilicon film, is plotted.

There are several possible physical mechanisms to cause this resistivity increase, such as polysilicon/oxide interface scattering, dopant segregation at the grain boundary, dopant leaching or loss, dopant segregation at the polysilicon/oxide interface, and changes in the number of carriers trapped into grain boundaries because of the grain-size. A detailed quantitative analysis will show that the dominant mechanisms causing the resistivity increase is the carrier trapping effect due to grain size reduction.

3.2. *Effective free carrier concentration of polysilicon thin films*

Fig. 2 shows the effective free carrier concentrations, measured from van der Pauw patterns, vs. the thickness of polysilicon films at room temperature. In this figure, it can be seen that: (1) the effective carrier concentrations of all samples decreased with the film thickness;

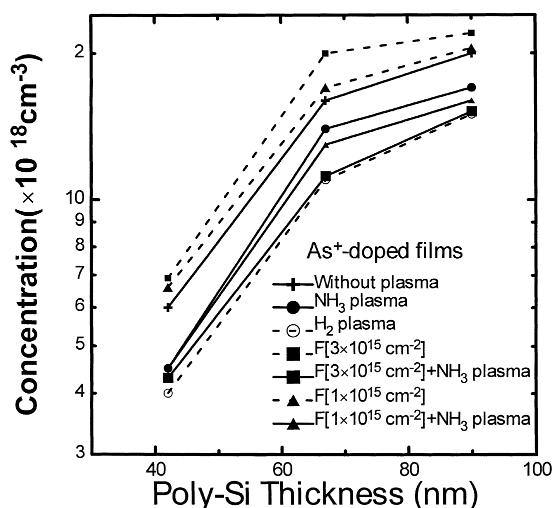

Fig. 2. The measured effective free carrier concentrations of plasma-hydrogenated or NH_3-treated and/or fluorine-implanted poly-Si film vs. the film thickness, respectively.

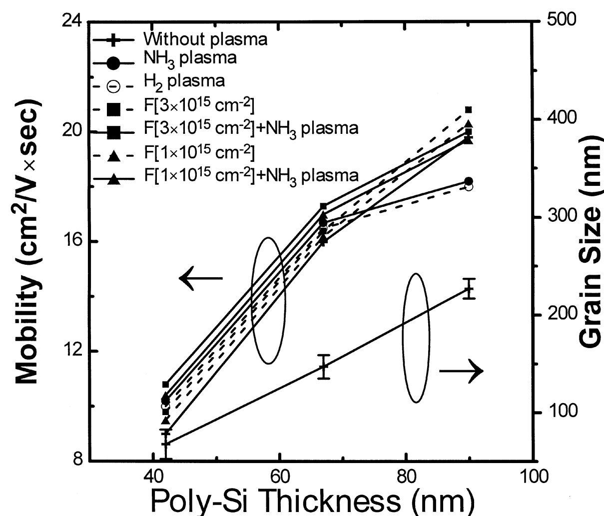

Fig. 3. The measured mobilities of plasma-hydrogenated or NH_3-treated and/or fluorine-implanted poly-Si film vs. the film thickness, respectively.

(2) all the effective carrier concentrations decreased after the plasma treatment; (3) the decrease was larger for the hydrogen plasma treated samples but smaller for the NH_3-plasma treated samples; (4) the decrease was larger for the thinner samples and smaller for the thicker samples; (5) the effective free carrier concentration of fluorine sample was higher than that of the non-fluorine samples; (6) the fluorinated sample had a large decrease; and (7) the decrease of higher fluorine dose (3×10^{15} cm^{-2}) sample was larger than that of lower fluorine dose (1×10^{15} cm^{-2}) sample. The above observations are consistent with the facts of Section 3.1.

The above facts explain why the resistivity of all samples increased after plasma treatments, i.e. the effective carrier concentrations decreased after plasma treatments. This is thought to be caused by neutralization of arsenic atoms by mono-atomic hydrogen [9,14]. The fluorinated samples had a greater neutralization effect than the non-fluorinated samples.

The fact that the effective carrier concentration decreased with the film thickness can be explained by the grain size of the films. As the thickness of film decreased, the size of the recrystallized grains during annealing was smaller. For the smaller grain size, the larger number of grain boundaries enhanced the precipitation of more arsenic atoms at grain boundaries, thereby reducing the effective free carrier concentrations. Also, the thinner samples were more easily neutralized by plasma treatments due to the same reason.

3.3. *Mobility of polysilicon thin films*

Fig. 3 shows the mobility plots, also measured from van der Pauw patterns, vs. the thickness of polysilicon

films for non-fluorinated samples and fluorinated samples, respectively. In these figures, the grain sizes, which were measured with TEM, are also plotted for comparison [12,14]. For the As implantation, the implant energy of the thicker thickness film was higher than that of thinner thickness film. This caused more amorphization for the thicker films and resulted in larger grain sizes for the films after recrystallization. Also, for the thinner samples, the film thickness limited growth of grains during recrystallization. Thus the grain sizes of the recrystallized film after annealing for the thinner samples were smaller than those of the thicker samples.

In the figure, it is observed that the mobility decreased with decrease of the thickness of the polysilicon film. This result can be easily explained by the grain size effect, i.e. thinner polysilicon films had smaller grain sizes, which consequently gave more grain boundaries, leading to more inter-grain potential barriers to decrease the mobility. In addition, as the film thickness became thinner, the surface scattering effect became more evident, which also decreased the mobility [19]. For the plasma-treated samples, the mobility increased for the thinner (< 60 nm) samples but decreased for the thicker (> 60 nm) samples after the treatments. The increase on the thinner films is believed to be due to the passivation effect of the hydrogen or NH_3 atoms (or molecules) on grain boundaries of the films to decrease inter-grain boundary potentials. However, as the film thickness was larger than 60 nm, this passivation effect is overridden by the neutralization effect of the plasma. The neutralized As atoms created higher inter-grain boundary potentials to degrade the film mobility.

In the plots, we see that fluorine-implanted samples had higher mobilities as compared to those of the un-implanted samples, and the higher the fluorine dosage (3×10^{15} cm^{-2}), the higher mobility. For thinner samples (< 60 nm), the samples with higher fluorine implant and with the NH_3 plasma treatment had the best mobility. Kim et al. [3] and Chern et al. [6] reported similar results on TFTs, i.e. the TFTs with higher fluorine implantation dosages had a better performance, and, a TFT with a thinner active layer (50 nm) exhibited a more significant improvement on its effective field mobility after the hydrogen plasma treatment as compared to those of thicker active layers (100 nm and 150 nm).

3.4. Activation energy of resistivity

The activation energies of resistivities vs. the thickness of each sample was measured and plotted in Fig. 4. As expected the activation energy exhibited exactly the opposite trend as did the mobility of Fig. 3, i.e. it decreased, with the increase of the polysilicon film thickness. For thicker polysilicon films, whose grain sizes were larger, they gave smaller activation energies [20–22]. Similarly, the fluorine-implanted samples had lower activation energies than those of the un-implanted samples and the higher the fluorine dosage (3×10^{15} cm^{-2}), the lower the activation energy. Also, the samples after plasma treatments had lower activations for the film thickness less than 60 nm, but had higher activation energies for the film thickness larger than 60 nm. Hence, the fluorine passivation effect is more effective for the thinner (< 60 nm) polysilicon films.

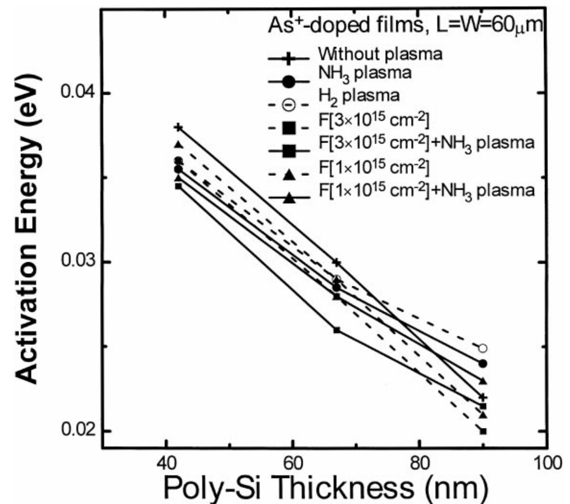

Fig. 4. The activation energy of resistivity of plasma-hydrogenated or NH_3-treated and/or fluorine-implanted poly-Si film vs. thickness, respectively.

3.5. TEM planar-view pictures

Some of the TEM planar-view pictures of the above samples are shown in Fig. 5a–c. They are bright-field pictures of the only As^+-doped, and the fluorine-implanted (1×10^{15} and 3×10^{15} cm^{-2}) samples (90 nm thickness), respectively. Comparing Fig. 5a with b and Fig. 5b with c, respectively, one finds that the fluorine-implanted sample had a larger grain size than that of the As^+-doped only sample and the higher fluorine-implanted sample had a larger grain size. This allowed the fluorine-implanted sample to have a larger mobility than that of the As^+-doped sample as mentioned in the previous section. The main reason for this grain size enlargement was that the fluorine implantation caused amorphorization of polysilicon films and, the more implantation dosage, the more amorphorization, leading to greater grain sizes for recrystallization. Another reason may be due to the retarded nucleation caused by the higher disorder of polysilicon network at the polysilicon/pad oxide interface as mentioned by Park et al. [7].

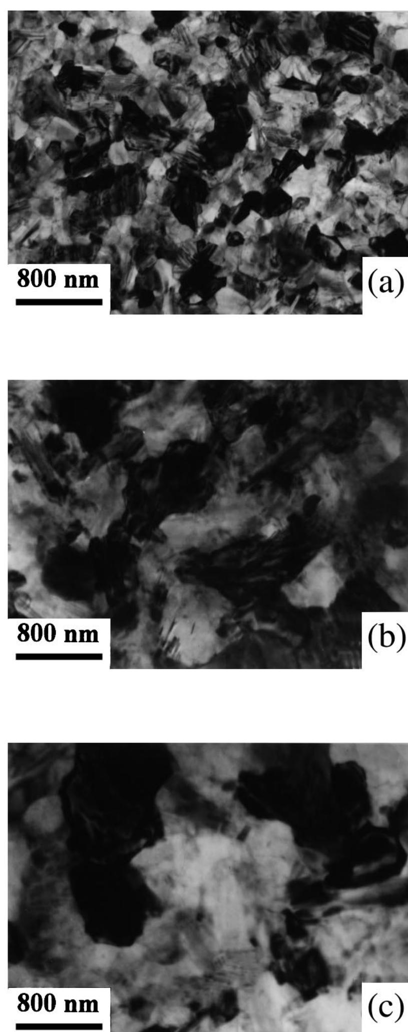

Fig. 5. The plane-view TEM pictures of the poly-Si films of 90 nm thickness for (a) As^+-doped, (b) fluorine-implanted (1×10^{15} cm^{-2}) on As^+-doped and (c) fluorine-implanted (3×10^{15} cm^{-2}) on As^+-doped, respectively.

4. Conclusions

From the above study, it can be concluded that: the resistivity of polysilicon thin film increases with decreasing the film thickness. The increase of the resistivity is mainly caused by the decrease of the grain size of the film since the thickness of the film limits the maximum grain size of the recrystallized film during the annealing process. The fluorine atoms passivate the defects of polysilicon films. This effect increases the carrier mobility, grain size and neutralization effects. The hydrogen or NH_3 plasma treatment on the film decreases the effective carrier concentration through the neutralization effect on arsenic ions, and this phenomenon is more evident for the thinner film. The plasma treatment decreases the mobility of the film, unless the thickness of the film is less than 60 nm, for which the plasma passivation effect becomes dominant. By jointly applying the fluorine-passivation and NH_3-plasma treatment into the polysilicon film, a high performance polysilicon film with a high mobility can be obtained.

Acknowledgements

The authors would like to acknowledge the financial support of the National Science Council of PR China through the contract NSC-83-0404-E009-017 for this research.

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