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A HEAT-RESISTING NEW AMORPHOUS-SILICON

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A new amorphous-silicon (a-Si), whose dangling bonds are terminated only by fluorine, is produced by the rf sputtering of silicon in mixtures of Ar and SiF_4 gases. n- and p-type doping of this fluorinated a-Si alloy (a-Si:F) is acheived by the addition of BF_3 and PF_5 in the sputtering gas. Annealing properties of the a-Si:F are studied to show that the a-Si:F is heat-resistant even after an annealing at 600 °C.

I. Introduction

An amorphous-silicon appears to be one of the most promising materials for wide area electronic devices such as low-cost solar cells. However, the utilization of the conventional hydrogenated a-Si alloy (a-Si:H) seems to be limited at the moment, since the hydrogen, as the terminator of dangling bonds, effuses from Si at temperatures as low as 350 °C [1]. Thus, it is important to find a new dangling bond terminator which does not effuse at such low temperatures. Fluorine appears most desirable for it, because the bonding energy of Si-F bond is greater than that of Si-H by as much as 60 %.

Ovshinsky et al. [2] have reported on the a-Si alloy containing both F and H (a-Si:F:H). However, in the present work, to make a heat-resisting a-Si, a new a-Si alloy whose dangling bonds are terminated only by F atoms is produced by the rf sputtering of Si in mixtures of Ar and SiF_4 gases. The F content and temperature dependence of dark conductivity of this a-Si:F are measured to know the reduction of dangling bonds due to the incorporation of F. n- and p-type doping is performed by the addition of BF_3 and PF_5 gas in the sputtering gas. The variation of infrared absorption spectra and temperature dependence of dark conductivity due to annealing process is observed. And it is found that the F atoms terminate dangling bonds sufficiently such that n- and p-type of the a-Si:F can be controlled by the incorporation of boron and phosphorous, and also that our a-Si:F is heat-resistant up to annealing temperature of 600 °C [3].

II. Experiments and Results

The deposition conditions of our a-Si:F are summarized in Table I. Here, T_S, p_{gas} and R_{SiF_4} refer to the substrate temperature, the sputtering gas pressure and the ratio of the partial gas pressure of SiF_4 to p_{gas}, respectively.

To know the amount of F incorporation, the F contents in the

Target	Intrinsic Si, $\rho > 1000\ \Omega cm$
Sputtering gas	Ar and SiF_4 mixture
P_{gas}	4×10^{-2}, 1.2×10^{-1} Torr
rf power	200 W/8 cmϕ target
R_{SiF_4}	0 ∿ 6 %
T_s	R.T. ∿ 500 °C
Deposition rate	2 ∿ 3 Å/sec
Substrates	Corning 7059, Fused silica for electrical measurement. Intrinsic crystalline Si for infrared absorption measurement Glassy carbon for backscattering measurement

Table I Deposition condition

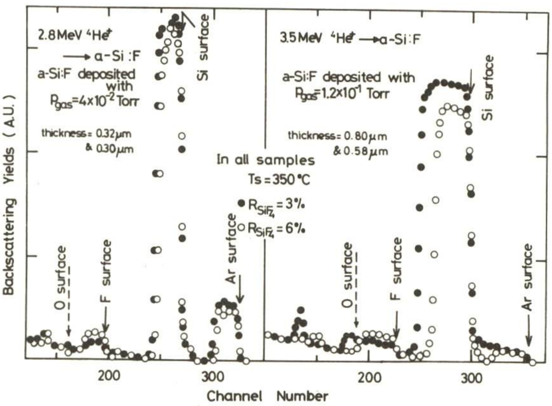

Fig. 1 Backscattering raw spectra

a-Si:F were measured by the Rutherford backscattering technique with $^4He^+$. The measured raw spectra are shown in Fig.(1) for samples deposited at T_s=350 °C and with both $P_{gas}=4 \times 10^{-2}$ and 1.2×10^{-1} Torrs. In the spectra, the surface positions of atomic species are indicated by solid arrows, together with the imaginary surface positions of oxygen indicated by dotted arrows. This figure shows that our a-Si:F consists of Ar, Si and F atoms but does not contain oxygen within experimental error (less than 2 atomic %), though the oxygen inclusion is sometimes observed in the a-Si sputtered only in Ar gas particularly when P_{gas} is high [4]. This figure also shows that the F content is proportional to R_{SiF_4}. For instance, the F content estimated from this figure is about 14 atomic % for samples of P_{gas}= 4×10^{-2} Torr, about 18 atomic % for those of $P_{gas}=1.2 \times 10^{-1}$ Torr when R_{SiF_4}=6 %, and decreases linearly from these values as R_{SiF_4} decreases.

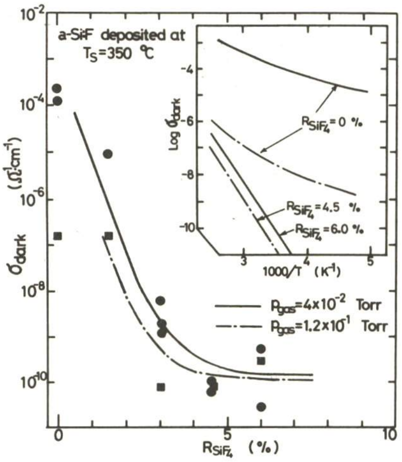

Fig. 2 R_{SiF_4} dependence

Next, to confirm the reduction of dangling bonds due to the incorporation of F atoms, we measured both R_{SiF_4}-dependence of dark conductivity σ_{dark} and temperature-dependence of σ_{dark}. Here, the conductivity is measured under the electric field of about 10^3 V/cm which is applied between two aluminum electrodes on the surface of a sample. The results are shown in Fig.(2) for the a-Si:F deposited with $P_{gas}=4 \times 10^{-2}$ Torr (Solid curves) and with $P_{gas}=1.2 \times 10^{-1}$ Torr (dashed and dotted curves). As seen in this figure, σ_{dark} is relatively high when R_{SiF_4}=0 % since the hopping transport through dangling bonds is dominant, but as R_{SiF_4} increases the σ_{dark} lowers. This impies that the number of dangling bonds reduces as R_{SiF_4} increases. The inset of Fig.(2) confirms this reduction. That is, as R_{SiF_4} increases the conduction mechanism changes from a variable range

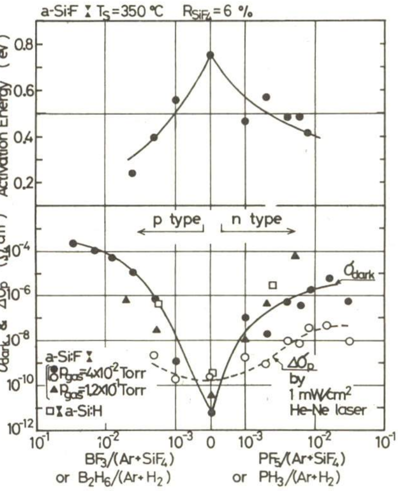

Fig. 3 Doping result

hopping type to an activated type one. These results lead a conclusion that the F terminates dangling bonds sufficiently such that the hopping conduction caused by dangling bonds can not be observed. For the samples deposited with p_{gas}=1.2x10^{-1} Torr, the σ_{dark} is low even when R_{SiF_4}=0 % because of the uncontrollable oxygen inclusion. However, when R_{SiF_4} is more than 3 %, the oxygen inclusion is negligible and the difference of p_{gas} causes no significant difference in the properties of the a-Si:F.

After confirming that F as well as H can terminate dangling bonds, we tried to control the conductivity and p-n type of the a-Si:F by substitutional doping of B or P. And the doping was acheived by adding BF_3 or PF_5 gas to the sputtering gas. Figure (3) shows the experimental results of σ_{dark} and its activation energy of the doped a-Si:F, as a function of the pressure ratio of BF_3 or PF_5 gas to the sputtering gas. p- and n-type was checked by the thermo-electric power measurement. The similar results, which were reported by Paul et al.[5] for the sputtered a-Si:H, are shown by using a symbol of open squares, as a function of the gas pressure ratio of B_2H_6 or PH_3 to the mixture of Ar and H_2 gases. The symbol of open circles refers to the photo-conductivity $\Delta\sigma_p$ of the a-Si:F, which was measured by a He-Ne laser of 1 mW/cm^2. In this figure, it is clearly demonstrated that p-n type and conductivity of the a-Si:F can be controlled by mixing dopant gases, and also that its controllability is comparable to that observed for the a-Si:H. These results lead again a conclusion that the F terminates dangling bonds so sufficiently that the conductivity and p-n type of the a-Si:F can be controlled.

Finally, we studied the annealing properties of the a-Si:F. Figure (4) shows the spectra of infrared absorption of the a-Si:F before and after annealing at 600 °C. Here, the absorption peaks indicated in the figure have been estimated as Si-F stretching modes of Si-F_3 asymmetric, Si-F_2 asymmetric and Si-F_2 or Si-F_3 symmetric vibrations [6]. The similar spectra due to Si-D stretching vibrations in the dueterated a-Si alloy (a-Si:D) are shown for comparison. The a-Si:D was produced by using the same sputtering system to that for the a-Si:F, but the mixture of Ar and 15 % D_2 gases was used as the sputtering gas. T_A expresses the annealing temperature. The annealing itself was carried out for 20 minutes in dry N_2 or Ar atmosphere. From this figure, it is clearly found that the Si-F bonds are kept

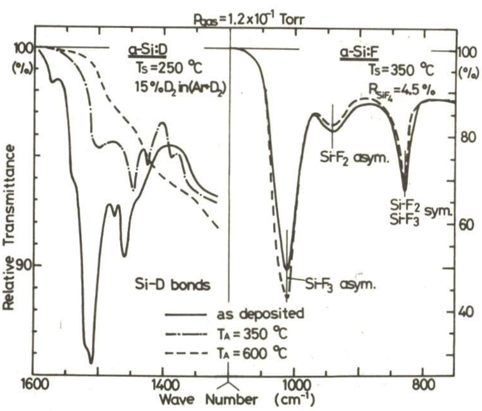

Fig. 4 Variation of infrared absorption spectra

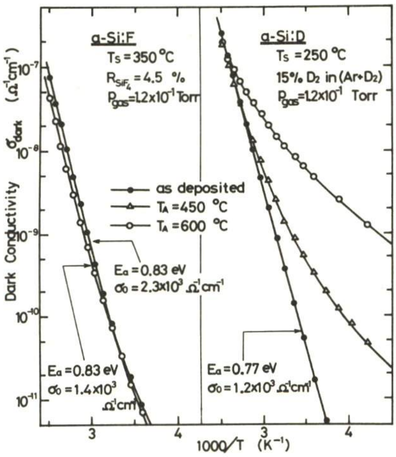

Fig. 5 σ_{dark}-1/T plots

almost unchanged after annealing at 600 °C, while the Si-D bonds start to change after annealing at 350 °C. This implies that the F atoms keep to terminate dangling bonds even after 600 °C annealing.

To confirm this, we observed the variation of σ_{dark}-reciprocal temperature (1/T) plots due to annealing process for both the a-Si:F and a-Si:D . The results are shown in Fig.(5). This figure shows that the conduction mechanism of the a-Si:F hardly changes even after 600 °C annealing, while that of the a-Si:D changes from the activated type to the variable range hopping type as annealing temperature increases. E_a and σ_0 in this figure express the activation energy of conduction and the pre-exponential factor, respectively. These values, particularly σ_0 values, suggest that the F atoms keep to reduce the dangling bonds sufficiently even after annealing. That is, our a-Si:F is heat-resistant up to annealing temperature of 600 °C.

III. Conclusions

From the above experimental results, we conclude as follows:

1) By using the rf sputtering of Si in mixtures of Ar and SiF_4 gases, an a-Si alloy whose dangling bonds are terminated only by F atoms can be produced.
2) The conductivity and p-n type of this a-Si:F can be controlled by the incorporation of substitutional impurities such as B or P. And the controllability of conductivity by doping B or P is comparable to that obtained for a sputtered a-Si:H.
3) This a-Si:F is heat-resistant at least up to the annealing temperature of 600 °C.

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