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B-4-2 Properties of a Fluorinated Heat-Resisting Amorphous-Silicon Containing no Hydrogen

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1.Introduction:

An amorphous-silicon (a-Si) is expected as one of the most promising materials for wide-area electronic devices. However, at the moment, the application of a conventional hydrogenated a-Si (a-Si:H) seems to be limited, since the a-Si:H changes its properties at the temperature as low as 350 °C,due to the decomposition of hydrogen (H) working as a dangling-bonds terminator. Thus, we tried to produce a new heat-resisting a-Si in which dangling-bonds are terminated only by fluorine (F), because F bonds with silicon (Si) more tightly than H as much as 60 % and hence F appears the most desirable new terminator. And we could succeed it by using the rf sputtering method in a mixture of Ar and SiF_4 gases. This paper presents how F terminates dangling-bonds without incorporating H at all and how heat-resisting this new fluorinated a-Si (a-Si:F) is. Additionally, this also presents the result of study to improve the properties of a-Si:F such as photo-conductivity.

2.Experiment and Results:

Conditions of deposition for a-Si:F are summarized in Table 1. Here, T_s and R_{SiF_4} express the substrate temperature and the ratio of the partial pressure of SiF_4 to the total pressure of sputtering gas, respectively.

At first, after measuring F content in a-Si:F by the Rutherford backscattering technique, we observed the infrared absorption, the temperature-dependence of conductivity σ and the photo-conctivity $\Delta\sigma_{photo}$, to study whether F worked as a dangling-bonds terminator as well as H. Particularly the structure of Si-F bonds was investigated by analyzing the infrared absorption spectra, to find the way to improve $\Delta\sigma_{photo}$. As results, it is found as follows; 1) F content in a-Si:F is proportional to R_{SiF_4}, and it is about 15 % for the sample deposited at R_{SiF_4}=6 %, 2) F forms Si-F, $Si-F_2$ and $Si-F_3$ bonds depending on R_{SiF_4}, and 3) F terminates dangling-bonds so enough that the hopping conduction due to the dangling-bonds can not be observed.

Thus, next, to know the magnitude of the termination of dangling-bonds by F and also to know the feasibility of the device application of a-Si:F, we tried to control the p-n type and σ of a-Si:F by doping the substitutional impurities such as Boron (B) or Phosphorous (P). The doping was carried out by mixing BF_3 or PF_5 gas with the sputtering gas, and σ and its activation energy were measured for the samples produced at the various ratios of BF_3 or PF_5 gas to the sputtering gas. Figure 1 shows the results for a-Si:F deposited at R_{SiF_4}=6 % and T_s=350 °C, together with the results of $\Delta\sigma_{photo}$ shown in a dotted curve. The photo-conductivity was measured here under the exposure of He-Ne laser of 1 mW/cm^2. The symbols ◎ express the similar results of the sputtered a-Si:H which was doped by PH_3 or B_2H_6, reported by Paul et al[1)]. The p-n type was determined by the thermo-electric power measurement. In this figure, it is clearly shown that the p-n type and σ

of a-Si:F can be controlled by the dope of B or P, and also that the doping efficiency is comparable with that of the sputtered a-Si:H. This shows that F terminates dangling bonds so sufficient that σ of a-Si:F is controlled by doping, and also this suggests the feasibility of a-Si:F as a new material for electronic devices.

Finally, we observed the variation of F content, infrared absorption spectra, temperature-dependence of σ and optical properties, due to annealing. And we found that all these were kept unchanged even after annealing at 600 °C at least. As an example, here, we show the results of the optical measurement in Fig. 2, comparing those with the similar results of both a-Si and a-Si:H. Both a-Si and a-Si:H were deposited using the same sputtering system to that for a-Si:F except the sputtering gas. The sputtering gas was a pure Ar and a mixture of Ar and 15% H_2 for a-Si and a-Si:H, respectively. T_s was 250 °C. This figure clearly shows that the optical properties of a-Si:F are kept unchanged after annealing more than 600 °C though those of a-Si and a-Si:H are changed at the temperature less than 400 °C. This means that our a-Si:F is heat-resisting as we expected.

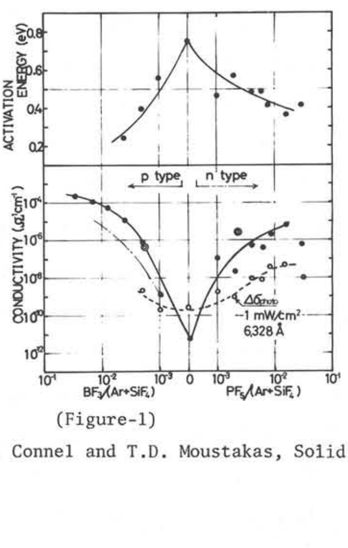
3.Conclusions:

As mentioned above, so far, we obtained the following conclusions: 1) By using the sputtering method , purely fluorinated a-Si can be produced without incorporating H at all. 2) The p-n type and the conductivity of this a-Si:F can be controlled by the dope of the substitutional impurities such as B or P. The doping efficiency is comparable with that of the sputtered a-Si:H. 3) This a-Si:F is heat-resisting. The properties of a-Si:F are kept unchanged after 600 °C annealing.

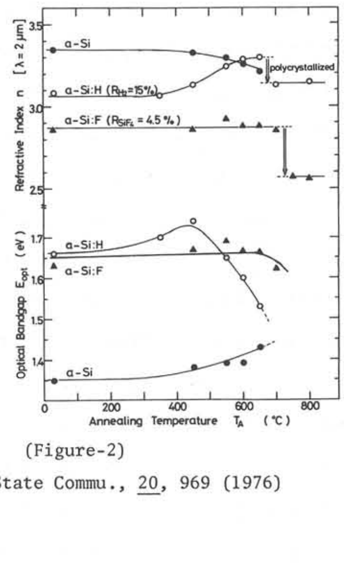
At the moment, the photo-conductivity and the doping efficiency of our a-Si:F are lower than those of the glow-discharged a-Si:H. But, we will present the results of studies to improve those, based on the analysis of the infrared absorption data.

Target	intrinsic c-Si
Gas pressure	4×10^{-2} Torr
Back pressure	3×10^{-7} Torr
rf power	200 W
R_{SiF_4}	0 - 6 %
T_s	R.T. - 500 °C
Depo. rate	2 - 3 Å/sec

(Table-1)



(Figure-1)



(Figure-2)

1) W. Paul, A.J. Lewis, G.A.N. Connel and T.D. Moustakas, Solid State Commu., 20, 969 (1976)