# STUDY OF HYDROGEN IN ANNEALED AMORPHOUS SILICON AND IMPLANTED AMORPHOUS CARBON

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## ABSTRACT

Hydrogen contents and its depth profiles, obtained by nuclear reaction induced by fluorine ion, have been investigated for a series of thermal annealed amorphous silicon and implanted amorphous carbon (diamond-like carbon) films. For dual layer amorphous silicon films, it is shown that hydrogen of either a-Si:H or a-SiN$x$:H sublayer moves obviously at different annealing conditions. For diamond-like carbon (DLC) films, measurements show that, by argon implantation, hydrogen contents decrease obviously with the increase of implanting dose. The decrease of hydrogen contents results in the decrease of diamond-like ($SP^3$) and graphite-like ($SP^2$) components of DLC films. But, the ratios of $SP^2$ and $SP^3$ increased, and the resistivities decrease with the increase of implanting dose.

**Key words:** Annealed amorphous silion Implanted amorphous carbon

## I. INTRODUCTION

Much interest has arisen recently[1-4] in r.f. plasma GD deposited thin films of silicon and carbon. Their chemical and physical properties make them promising materials for various electronic and optical applications. These properties of films vary with the hydrogen contained in the films.

In this paper, we report results on the moves of hydrogen profiles in the interface of dual layer a-Si:H/a-SiN$x$:H and a-SiN$x$:H/a-Si:H films after thermal annealing process and on the changes of hydrogen contents in the a-C:H films after argon ion implantation. The hydrogen was measured by using nuclear reaction analysis (NRA) technique.

## II. SAMPLE PREPARATION

The amorphous silicon films were provided by Shanghai Institute of Ceramics. Considering the influences of depth resolution of NRA at large depth, we deposited two dual layer a-Si:H/a-SiN$x$:H/ silicon and a-SiN$x$:H/a-Si:H/ silicon ($x=0.85$) films at $T_s=250$ °C by using equipped shutter deposition system. The thickness of each sublayer is about 60nm. All films were then annealed in vacuum for one hour at two temperatures: $T_a=300$ °C and 430 °C.

Deposition of the amorphous carbon films were performed by r.f.plasma GD with ($CH_4+H_2$) mixed gas at the conditions of $T_s=250$ °C and $W=25$W. Thicknesses of the films are about 300nm. These films were then implanted by 140keV argon ions to various doses: $5\times10^{13}$, $1\times10^{15}$ and $2\times10^{16}$Ar/cm$^2$ in ULVAC IM-200M implanter of Ion Beam Laboratory of Shanghai Institute of Metallurgy.

## Ⅲ. RESULTS AND DISCUSSIONS

The experiments were done on 2× 1.7 MV tandem accelerator of Lanzhou University. Nuclear reaction $^1H(^{19}F,\alpha\gamma)^{16}O$ ($E_{res}=6.42$ MeV) was used to determine the depth profiles of hydrogen. Fig.1 illustrates the hydrogen profiling technique, and $\gamma$ ray yield is plotted against the energy of the incident $^{19}F$ ions. Fig.2 shows the hydrogen profiles in dual layer films after thermal annealing process. It is obvious that hydrogen of either a-Si:H or a-SiNx:H sublayer moves towards shallow region at temperature 300 °C, and towards deep region at temperature 430 °C. After annealed at 300 °C, some hydrogen was released from films, so the total hydrogen content was decreased. But it is not clear why hydrogen content increases after annealing at 430 °C as shown in Fig.2 (b).

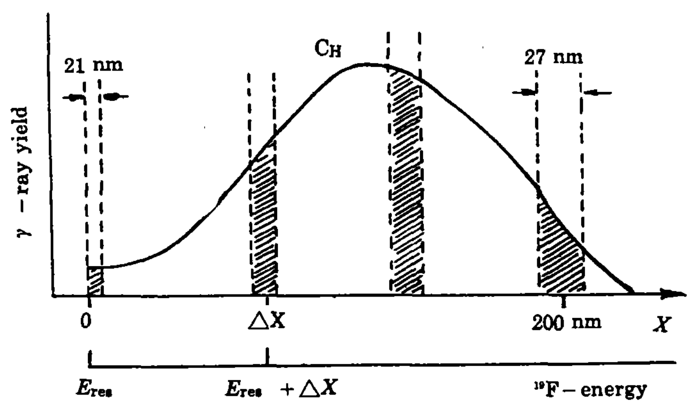
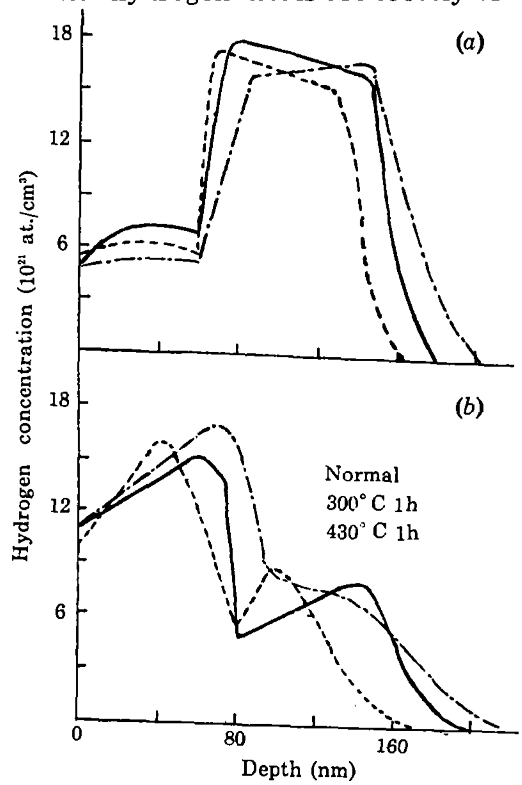



**Fig.1 Illustrates the nuclear technique of measuring the hydrogen content**

The observed $\gamma$ -ray yield is potted against the energy of the $^{19}$F ions

For DLC films, it is known that they can contain loosely bounded and free stated hydrogen[5] which are rapidly lost under ion beam bombardment. Fig.3 shows the hydrogen contents of a DLC film without argon implantation varied with the irradiation doses of incident fluorine at two beam currents. It is obvious that hydrogen release of DLC film is smooth and simply linear with the fluorine fluence at small incident beam current (~ 2nA). But under large beam bombardment (~ 20nA), hydrogen content is rapidly lost according to an exponential function, and the asymptotic value of exponential function is related to the hydrogen atoms tightly bounded in the film. Therefore, from curve (*b*) of Fig.3, we can give an indication to whether hydrogen atoms are loosely or tightly bounded in the film.



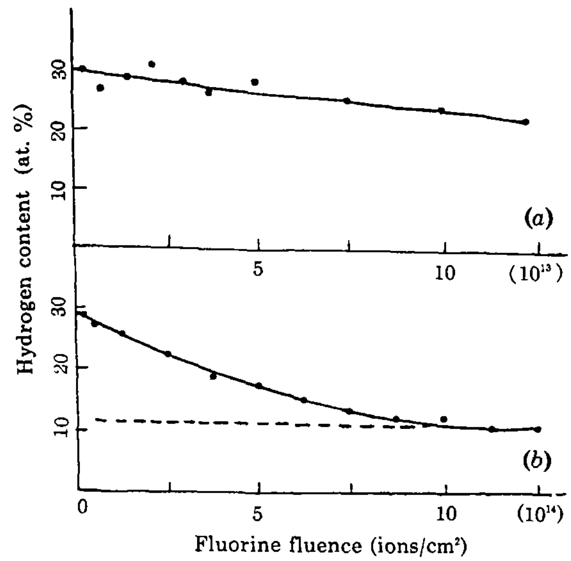




**Fig.2 Hydrogen profiles for two specimens showing the influence of thermal annealing temperature**

a. a－Si:H/a－SiNx:H/Silicon films

b. a－SiNx:H/a－Si:H/Silicon films

**Fig. 3 Hydrogen content of DLC film measured as a function of irradiation doses with 6.25 MeV $^{19}$F at two beam currents of incident fluorine ion** (*a*) ~ 2nA and (*b*) ~20nA

During the measurements of hydrogen contents, the DLC films were bombarded by fluorine ions with small beam current (~ 2nA) for five minutes. Hydrogen contents of two depth (50nm and 150nm) in the films were measured. The latter depth is corresponding to the projected range of 140 keV argon implantation. The results are shown in the Fig.4. For the same film, the changes of infrared spectra and resistivities with the doses of argon implantation (see Fig.5) were studied. From the analysis of infrared spectra, we found that diamond－like ($SP^3$) and graphite－like ($SP^2$) components are both decreased, with the increases of doses of argon implantation. Meanwhile, the ratio of $SP^2/SP^3$ components increased with the increases of argon doses. So resistivities of the films decrease with the increase of argon doses. All this is associated with the hydrogen release from the films due to the irradiation of argon ions. The loss of hydrogen in the DLC films can be explained by considering that covalent C – H structure is destroyed, bounded and ﹨e stated hydrogen atoms removed during ion implantation.

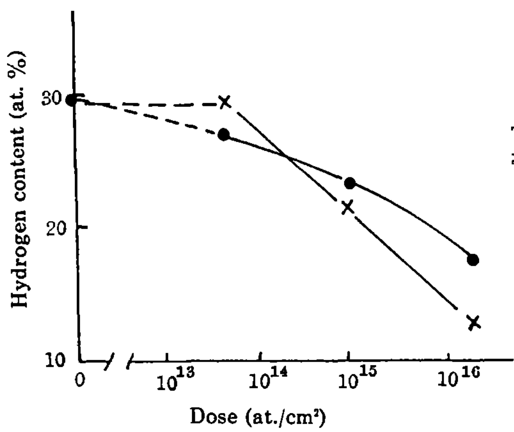



**Fig.4 Hydrogen content of two depth versus doses of argon implantation for DLC films: 50 nm (X) and 150 nm (●)**

The latter depth is corresponding to the projected range region of 140 keV argon ion in DLC films

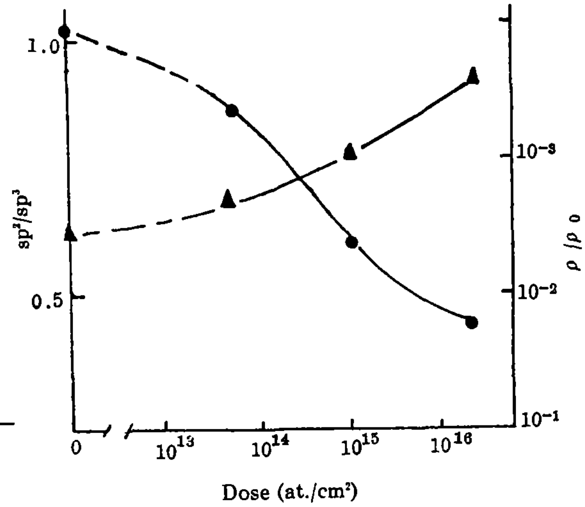



**Fig.5 Dependence of resistivity (●) and $SP^2/Sp^3$(▲) of DLC films on doses of argon implantation**

## Ⅳ. CONCLUSIONS

It is shown that hydrogen of either a – Si:H or a – SiN$x$:H sublayer moves obviously at different annealing temperatures in super – lattice amorphous silicon films. Hydrogen contained in diamond – like carbon films is not stable under the bombardment of 140 keV argon or 6.52 MeV fluorine ions. With the increasing doses of argon implantation, the hydrogen bounded and free stated in DLC films is released. When hydrogen contents decrease, the diamond – like component is down rapidly compared with graphite – like component, and thus the resistivities of DLC films are also decreased with the increases of argon ions implantation.

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