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Hydrogen loss and its improved retention in hydrogen plasma treated a-SiN$_x$:H films: ERDA study with 100 MeV Ag^{7+} ions

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ABSTRACT

Hydrogen loss from a-SiN$_x$:H films under irradiation with 100 MeV Ag^{7+} ions using elastic recoil detection analysis (ERDA) experiment is reported. The results are explained under the basic assumptions of the molecular recombination model. The ERDA hydrogen concentration profiles are composed of two distinct hydrogen desorption processes, limited by rapid molecular diffusion in the initial stages of irradiation, and as the fluence progresses a slow process limited by diffusion of atomic hydrogen takes over. Which of the aforesaid processes dominates, is determined by the continuously evolving Hydrogen concentration within the films. The first process dominates when the H content is high, and as the H concentration falls below a certain threshold ($H_{critical}$) the irradiation generated H radicals have to diffuse through larger distances before recombining to form H_2, thereby significantly bringing down the hydrogen evolution rate. The ERDA measurements were also carried out for films treated with low temperature (300 °C) hydrogen plasma annealing (HPA). The HPA treated films show a clear increase in $H_{critical}$ value, thus indicating an improved diffusion of atomic hydrogen, resulting from healing of weak bonds and passivation of dangling bonds. Further, upon HPA films show a significantly higher H concentration relative to the as-deposited films, at advanced fluences. These results indicate the potential of HPA towards improved H retention in a-SiN$_x$:H films. The study distinguishes clearly the presence of two diffusion processes in a-SiN$_x$:H whose diffusion rates differ by an order of magnitude, with atomic hydrogen not being able to diffuse further beyond ~ 1 nm from the point of its creation.

1. Introduction

Sub stoichiometric silicon nitride thin films deposited by plasma enhanced chemical vapour deposition technique (PECVD) find wide range of applications like device passivation [1], LEDs [2], ARCs [3,4] for solar cells [5] and devices [6]. Due to the use of precursor gases like silane (SiH_4) and ammonia (NH_3) these films have an inevitable presence of hydrogen in them, which leads to the popular nomenclature of 'PECVD silicon nitride' as 'amorphous hydrogenated silicon nitride' and abbreviated as 'a-SiN$_x$:H'. The process induced hydrogen incorporated in these films plays a crucial role in its microstructural [7], electronic [8] and optical properties [9,10]. Hydrogen effusion from a-SiN$_x$:H is relevant to many post processing steps like UV exposure [11], high temp annealing [12], rapid thermal annealing [13–15], contact firing step in solar cell passivation [16,17], swift heavy ion irradiation, EUV irradiation [18]. In the past the study of loss of hydrogen from materials like a-C:H [19], a-Si:H [20], a-Si:C:H [21] and organic polymers [22] have been reported. In these reports, hydrogen loss has been widely accepted to take place predominantly in molecular form rather than in the atomic form. The release basically follows a single exponential decay or a combination of them depending on the microstructure and composition of the matrix hosting hydrogen. Accordingly, various models [23] to suit the particular case of these materials have been suggested.

Presently, we investigate the hydrogen release processes for the specific case of as-deposited and hydrogenated a-SiN$_x$:H thin films during elastic recoil detection analysis [24] (ERDA) measurements employing 100 MeV Ag^{7+} beam. It must be noted that irradiation with energetic (~MeV) ions offers a controlled and reproducible means of effecting hydrogen release from materials under extreme conditions, wherein, energy deposition can be varied in a wide range by the choice of the ion and its energy, in contrast to the conventional thermal treatments. The energy deposition of the ions into a-SiN$_x$:H thin films are understood on the basis of thermal spike model. The present article discusses various factors that determine the release of hydrogen during MeV ion irradiation.

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In the past, hydrogen release from *a*-SiN_x:H deposited by various growth methods like Hotwire CVD [25], ECR Plasma deposition [14], reactive evaporation [26] and PECVD [12] have been reported. These reports have employed various thermal treatments like RTA or furnace anneals, which are quite distinct from the ion irradiation process. However, the detailed study of the effect of stoichiometry on effusion of hydrogen from the *a*-SiN_x:H films during ERDA with MeV ion irradiation is being reported for the first time to the best of our knowledge. Furthermore, the study is extended to films subjected to low temperature Hydrogen plasma annealing (HPA), wherein, an order of magnitude improvement in H retention under MeV irradiation is observed. The improvement is attributed to the remarkable healing of the *a*-SiN_x:H network during low temperature HPA. These results are technologically relevant for the passivation applications *a*-SiN_x:H.

2. Experimental details

Silicon nitride (*a*-SiN_x:H) thin films were deposited on p-type Si (1 0 0), by conventional PECVD (Model: SAMCO PD-2S) technique. This system uses RF (13.56 MHz) power to maintain a glow discharge and produce ionized species necessary for thin film growth. Silane (SiH_4, 4% in Ar) and ammonia (NH_3) were used as precursor gases. The partial pressure ratio $P_r = P_{SiH_4}/P_{NH_3}$ of the reactant gases was varied to deposit films of different stoichiometries, which are named as S1, S2, S3, S4 and S5 hereafter. The Si content decreases from film S1 to S5. The other deposition parameters namely substrate temperature, chamber pressure and plasma power were maintained at 200 °C, 1 mbar and 25 W respectively. Further, the deposition time was varied in order to limit the thickness of the layers to ~100 nm. Low-temperature HPA was carried out for one hour at three different temperatures (250 °C, 300 °C and 350 °C) in the PECVD system. During HPA, the pressure, RF power and hydrogen flow were kept at 2 mbar, 25 W and 10 sccm respectively. Rutherford Backscattering Spectrometry (RBS) experiments were carried out using 1.7 MeV He^{2+} ions at a backscattering angle of 170°. The detector solid angle was 3.052 milli-steradians and its resolution was 17 keV. The concentration (atoms/nm3) of hydrogen in both as-deposited and HPA films was measured by the ERDA technique using 100 MeV Ag^{7+} ions. ERDA experiments were carried out in a vacuum of 4.5×10^{-6} mbar and a collimated beam of silver ions of a beam area of $\sim 1 \times 1$ mm^2 was made to impact at an angle of 20° with respect to the film surface. A beam current of 200–250 μA was employed. It was verified that the sample temperature does not exceed beyond 50 °C as per the formula illustrated by Ullersma et al. [21] The hydrogen recoils from the films were detected in a silicon surface barrier detector (SSBD) kept at 30° recoil angle with a polypropylene stopper foil in front of it to stop other recoils like nitrogen (N), oxygen (O) and silicon (Si). It may be noted here that in separate experiments, not reported here, it has been found through RBS measurements, that there is negligible loss in sample stoichiometry (N/Si) in the course of swift heavy ion irradiation.

3. Results and discussion

Table 1 lists the various details of the samples used for the ERDA experiments. It should be noted that all the samples have comparable thickness. Fig. 1 shows the results of ERDA measurement on the *a*-SiN_x:H thin films S1 to S5, wherein there is a change in stoichiometrygoing from S1 to S5 (see Table 1). The data basically represents the hydrogen recoils (atoms/cm^2) from *a*-SiN_x:H films upon irradiation with 100 MeV Ag^{7+} ions.

The obtained data representing the counts from the ERD detector are normalized according to the thicknesses (see Table 1) of the films in order to obtain the Hydrogen concentration per cubic nanometer. The H concentration in atoms/nm^3 will be denoted by ρ_H henceforth. There are several points to be noticed from Fig. 1. Firstly, it may be noted that all the decay profiles (plotted on a logarithmic y axis) are seen to be composed of two linear regions thereby indicating the presence of two

Table 1
Details of samples used for the hydrogen loss study.

Sample	N/Si	Thickness (nm) ± 0.1	Density* gm/cc	R_{eff}** (nm)	[H] at % (± 1)
S1	0.3	109.6	1.72	1.33	26
S2	0.5	117.8	1.61	1.42	31
S3	1.0	91.7	1.73	1.32	32
S4	1.1	116.8	1.90	1.2	29
S5	1.3	127.5	1.98	1.15	37

* Film densities as determined from the critical angle obtained in X-ray reflectivity measurements.
** Calculations from [28].

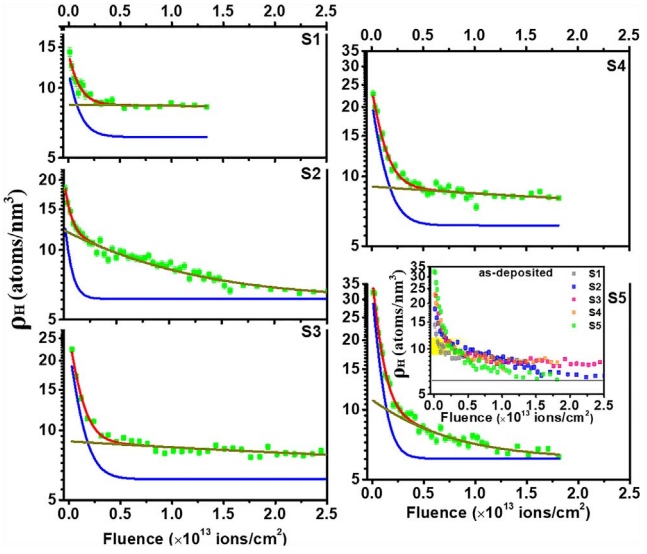

Fig. 1. Hydrogen concentration profiles as measured in the ERDA experiment for as-deposited *a*-SiN_x:H thin films S1 to S5 and their fitting with two exponentials decays, which represent different hydrogen release mechanisms. Inset shows the data overlapped on one another, wherein the yellow strip indicates the H concentration below which the H release slows down significantly.

hydrogen loss regimes. A fast mechanism dominates at fluence below ~10^{12} ions/cm^2 whereas a slow release dominates at higher fluences. ERDA data for hydrogen loss can be fit with a double exponential describing the aforementioned decays:

$$N(\varnothing) = y_o + N_1 e^{-K_1 \varnothing} + N_2 e^{-K_2 \varnothing} \quad (1)$$

N(∅) is the hydrogen concentration at any given fluence (∅), y_o represents the background noise. N_1 and N_2 are the H concentrations associated with each of the evolution processes. The sum, $N_1 + N_2$ gives the initial hydrogen content of the films prior to irradiation. K_1 & K_2 represent the rate constants for the two decay mechanisms. Secondly, the decay rates for these apparently independent mechanisms undergo change as the film composition varies from Si rich to stoichiometric. This indicates clearly a difference in diffusion constant of H as the films composition changes. In the later sections of this article we will try to understand the Hydrogen diffusivity through *a*-SiN_x:H films as the films composition (N/Si) on one extreme (S1) approaches a-Si and silicon nitride (S5) on the other end. Further, we will also investigate the conditions that determine the passage from one decay process to the other. The factors responsible for the asymptotic decay of H content to high fluences, following the initial rapid depletion will also be discussed.

Ion matter interactions in *a*–SiN_x:H: In order to understand the presently obtained data let us first take a brief survey of the current understanding of the hydrogen release processes. In general, the thermal/UV/MeV-ion based excitation of the hydrogenated materials