HYDROGENATION OF AMORPHOUS SILICON NITRIDE*

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ABSTRACT

A relationship between hydrogen and the equilibrium positive charge in silicon nitride films has been confirmed by rehydrogenation of annealed films using a hydrogen plasma. The primary relation between hydrogen and silicon-nitride charge is associated with Si-H formation.

INTRODUCTION

Previous experiments have shown that several atomic percent hydrogen is incorporated in chemical vapor deposited (CVD) silicon nitride (SiN_x) films prepared for MNOS (Metal or Si-gate/nitride/oxide/Si) memory device applications.[1-4] The total hydrogen concentration and the relative concentrations of N-H and Si-H bonds are dependent on the ammonia:silane flow ratio and deposition temperature.[1,4] Subsequent heating of films above the deposition temperature, which is typically 700 to 900°C, results in hydrogen loss by trap-limited diffusion.[4] Depositions of SiN_x for p-channel MNOS are usually performed at temperatures between 700 and 750°C because there is more equilibrium positive nitride charge, Q_{NC}, at these lower temperatures which gives negative equilibrium flat-band and threshold voltages. However, post deposition annealing at either MOS or Si-gate processing temperatures causes degradation of SiN_x properties, particularly for films deposited at these lower temperatures.

Parallels in the dependence of Q_{NC} and hydrogen on deposition and annealing characteristics have been noted previously;[1,5] however, many simultaneous effects occur during deposition and annealing. Methods for introducing hydrogen into SiN_x with minimum disturbance of the structure are thus required to establish the relationship between Q_{NC} and hydrogen. In the present paper we report studies in which hydrogen was introduced into annealed SiN_x films by exposure to a low pressure hydrogen plasma at temperatures between 300 and 700°C. Infrared absorption, nuclear reaction analysis, and capacitance-voltage measurements were used to investigate the reintroduction of hydrogen and to determine the relationship between Q_{NC} and hydrogen in SiN_x.

EXPERIMENTAL DETAILS

Silicon nitride films were deposited onto n-type Si substrates from NH_3 and SiH_4 mixed with N_2 carrier gas in an AMV 1200 reactor. Flow ratios of 100:1 and 200:1 for NH_3:SiH_4 and substrate temperatures between 700 and 775°C were used to achieve

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the desired Q_{NC} and chemical bonding of hydrogen. Isochronal (20 min.) annealing was performed in flowing N_2 at temperatures between 750 and 975°C, and radiative heating of samples in a tesla-coil-generated hydrogen plasma at $\sim$ 2 torr was used for rehydrogenation of SiN_x after annealing.

Nuclear reaction analysis (NRA) with the $^1H(^{15}N,(\alpha,\gamma)^{12}C$ reaction (depth resolution of $\sim$ 100 Å) was used to measure the hydrogen depth distribution and concentration before and after plasma hydrogenation. Chemically-bonded hydrogen was determined from Si-H and N-H stretch modes measured by the multiple internal reflection (MIR) technique, and Q_{NC} (assumed proportional to flat-band voltage) was determined from 1 MHz capacitance-voltage (C-V) measurements which were made by using a mercury probe on SiN_x films deposited on Si MIR plates.

RESULTS AND DISCUSSION

Chemically-bonded hydrogen and the C-V characteristics after successively higher annealing temperatures are shown in Fig. 1 for 1000 Å of SiN_x deposited from a 100:1 NH_3:SiH_4 ratio at 750°C onto a <100> Si (MIR) plate. The similarity between the reduction of chemically-bound hydrogen and the shift of the C-V characteristic toward zero (reduction of Q_{NC}) is apparent from these data.

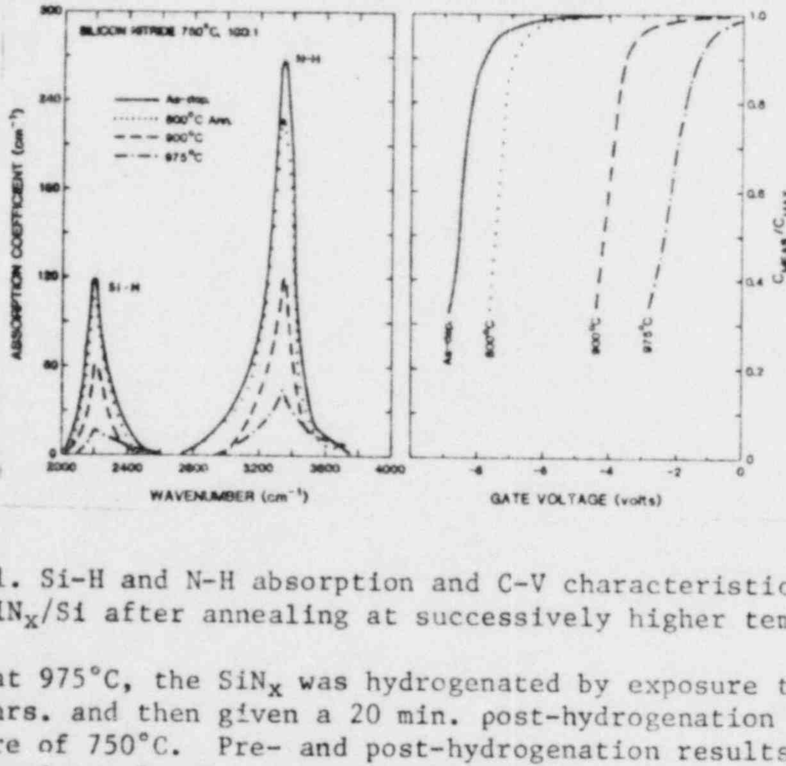

Fig. 1. Si-H and N-H absorption and C-V characteristics for CVD SiN_x/Si after annealing at successively higher temperatures.

After annealing at 975°C, the SiN_x was hydrogenated by exposure to a hydrogen plasma at 650°C for 17 hrs. and then given a 20 min. post-hydrogenation anneal at the deposition temperature of 750°C. Pre- and post-hydrogenation results are compared in Fig. 2. The comparison clearly shows rebonding of hydrogen during plasma exposure. No hydrogenation occurred in an exposure to H_2 at 650°C in the absence of a plasma. The sharpening of the C-V characteristic produced by hydrogenation indicates hydrogen passivation of interface states, and the large negative shift of the C-V characteristic substantiates a relationship between Q_{NC} and hydrogen.

Effects of temperature during plasma treatment are illustrated in Figs. 3 and 4. The data in Fig. 3 show that the intensities of Si-H and N-H absorption bands are largest after 300°C hydrogenation and decrease with increasing temperature. After 750°C annealing, however, the maximum intensities for the bands occur for films hydrogenated at 650°C. These apparently contradictory temperature effects are explained by the hydrogen concentrations and profiles measured by NRA as shown in Fig. 4. The NRA measurements were performed on 800 Å films annealed at 900°C prior

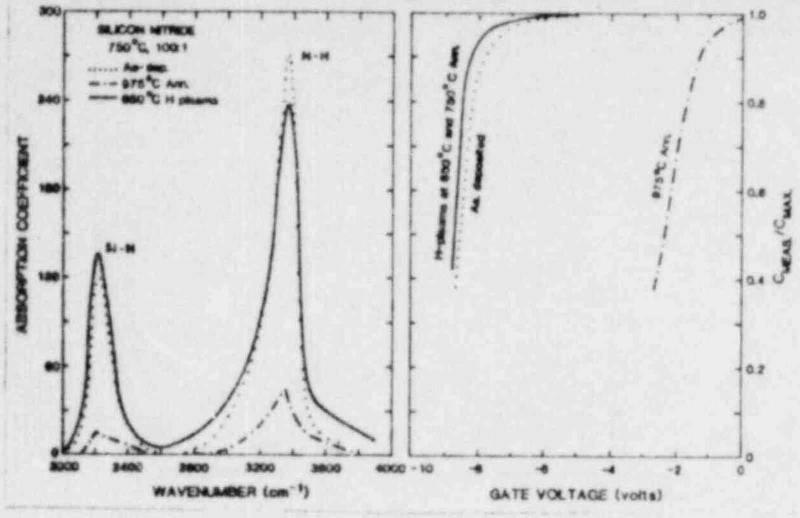

Fig. 2. Chemically bound hydrogen and C-V characteristic after 650°C plasma hydrogenation of annealed SiN_x (solid line). The as-deposited and final anneal data from Fig. 1 are included for comparison.

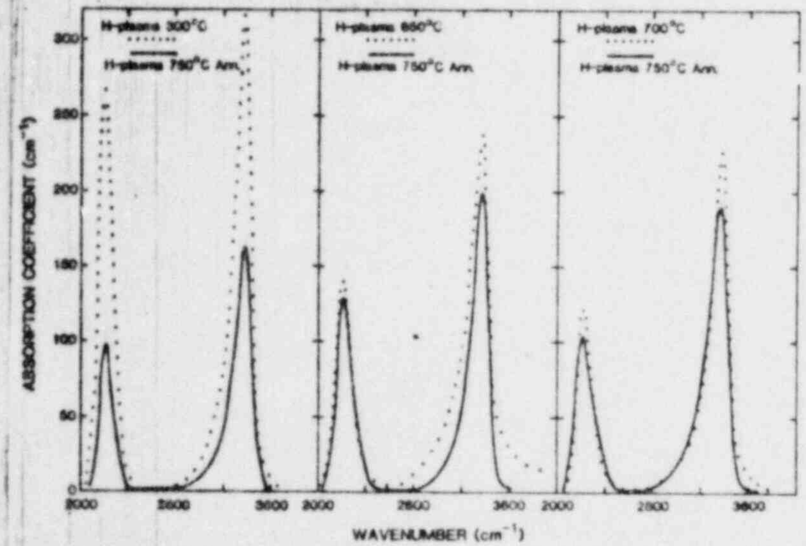

Fig. 3. Plasma treatment temperature effects on hydrogenation of annealed SiN_x as measured by Si-H and N-H absorption before and after 750°C anneal.

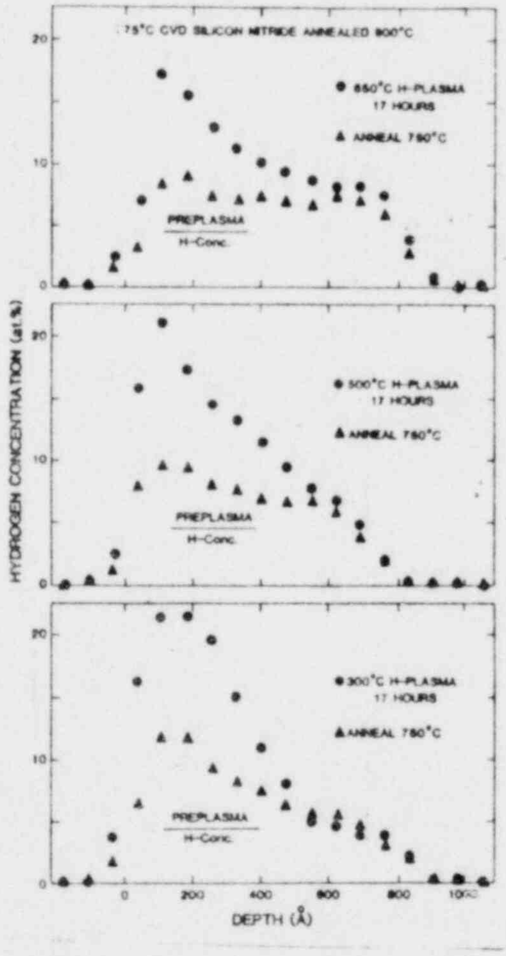

Fig. 4. Effect of plasma treatment temperature on hydrogenation of annealed SiN_x as measured by nuclear reaction analysis before and after 750°C annealing.

to hydrogenation. As can be seen from the data in Fig. 4, hydrogenation at 300°C produces a high concentration of hydrogen near the front surface. Back diffusion at 750°C of this near-surface hydrogen is a major factor in the large decrease in N-H and Si-H intensities produced by annealing. Little or none of the hydrogen introduced in the plasma at 300°C migrates through the film and therefore has little effect on Q_{NC}. On the other hand, hydrogenation at 650°C followed by annealing at 750°C gives a nearly uniform profile with approximately the as-deposited hydrogen concentration and restores the as-deposited C-V characteristic.

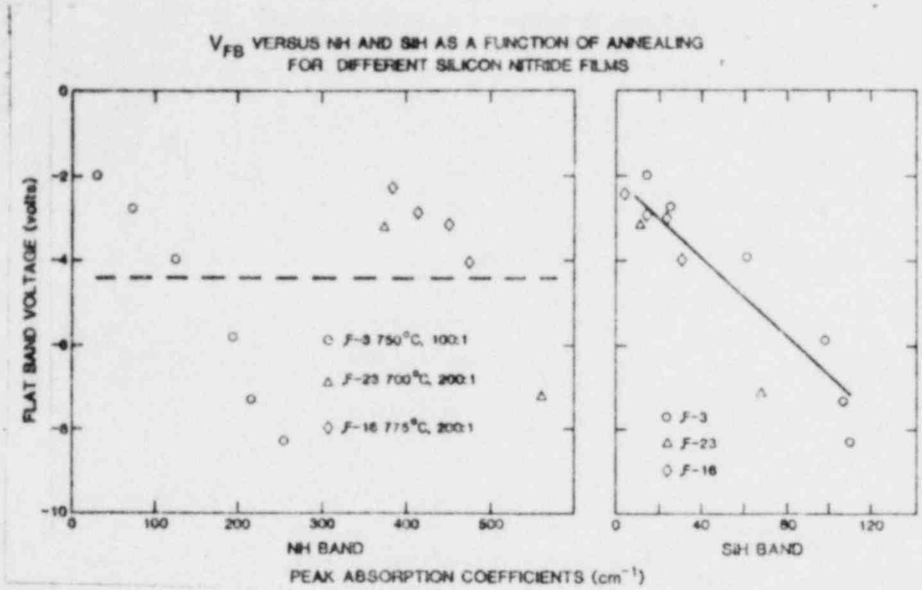

Fig. 5. Flat-band voltage normalized to 1000 Å film thickness plotted versus peak intensities for N-H and Si-H for SiN_x films which have a wide range of N-H and Si-H concentrations.

Although rehydrogenation of SiN_x by exposure to a hydrogen plasma and a dependence of Q_{NC} on hydrogen are well demonstrated by the results presented above, these data do not distinguish between Si-H and N-H centers for altering Q_{NC}. Plotted in Fig. 5 are flat-band voltage V_{FB} (voltage for $C = 0.7\ C_{meas}$) versus N-H and Si-H intensities obtained from annealing SiN_x deposited under conditions which yield a wide range in N-H and Si-H concentrations. These results show the same V_{FB} (and hence the same Q_{NC}) for a factor of four increase in N-H concentration which occurs when increasing NH_3:SiH_4 from 100:1 to 200:1. In contrast, the V_{FB} versus Si-H data show a functional similarity for the different SiN_x materials. From these results we conclude that the primary hydrogen-Q_{NC} relation occurs via the Si-H centers.

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