H2 dilution effect in the Cat-CVD processes of the SiH4/NH3 system

Abstract
Gas-phase diagnostics in the catalytic chemical vapor deposition processes of the SiH4/NH3/H2 system were carried out to examine the effect H2 dilution. The decomposition efficiency of NH3 showed a sharp decrease with the introduction of a small amount of SiH4, but this decrease was recovered by the addition H2 when the NH3 pressure was low. On the other hand, at higher NH3 pressures, the decomposition efficiency showed a minor dependence on the H2/ partial pressure. The addition of SiH4 to the NH3 system decreases the H-atom density by an order of magnitude, but this decrease is also recovered by H2 addition. H atoms produced from H2 must re-activate the catalyzer surfaces poisoned by SiH4 when the NH3 pressure is low.

I. Introduction
Catalytic chemical vapor deposition [Cat-CVD], often called hot-wire CVD, is one of the most promising techniques for preparing thin amorphous silicon nitride (SiNx) films at low substrate temperatures using SiH4 and NH3 as material gases. SiNx films thus prepared can be used as gas- and water-resistant coatings for organic and inorganic devices and as interlayer insulating films for microelectronic devices. One of the problems in this technique has been the low decomposition efficiency of NH3 in the presence of SiH4.

In the absence of SiH4, NH3 can be decomposed to NH; and H with a decomposition efficiency of more than 50%. However, the decomposition efficiency decreases sharply upon the introduction of a small amount of SiH4. This decrease has been attributed to the poisoning of the catalyzer surfaces by SiH4. Separating the catalyzers, one to decompose NH, and another to decompose SiH4 is not easy because the diffusional rate of SiH4 is large under low pressure conditions, such as those employed in conventional low-pressure CVD processes, and the prevention of catalyzer poisoning is difficult.

Recently, it has been found that the addition of H2 improves not only the
decomposition efficiency of NH₃ in the presence of SiH₄ but also the SiNx film quality. For example, Malian et al. have shown that the content of N atoms in the films increases significantly with H₂ dilution for a given NH₃/SiH₄ gas flow ratio. H₂ dilution also causes a reduction in the amount of N-H bonding in SiNx films. Wang et al. have demonstrated that near perfect conformal surface coverage can be obtained on a 100-nm-scale object [6]. In the present work, a systematic study was carried out to determine the catalytic decomposition efficiency of NH₃ in the SiH₄/NH₃/H₂ system. Such information is essential for optimizing of the deposition conditions to prepare SiNx conformal films. The absolute H-atom densities were also measured under several conditions.