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Effect of NH_3 flow rate on growth, structure and luminescence of amorphous silicon nitride films by electron cyclotron resonance plasma

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Abstract

In this paper, hydrogenated amorphous silicon nitride (a-SiN_x:H) films have been deposited using an electron cyclotron resonance chemical vapor deposition system. The effect of NH_3 flow rate R on the deposition rate, structure and luminescence were studied using various techniques such as optical emission spectroscopy, Fourier Transform Infrared absorption (FTIR), X-ray photoelectron spectroscopy (XPS) and fluoro-spectroscopy, respectively. Optical emission behavior of SiH_4+NH_3 plasma shows that atomic Si radical concentration determines the film deposition rate. Structural transition of a-SiN_x film from Si-rich one to near-stoichiometric/N-rich one with R was revealed by FTIR and the two phase separation of a-Si and a-Si_3N_4 was also convinced in Si-rich SiN_x films by XPS. Either photo- or electroluminescence for all the SiN_x films with $R>3$ sccm shows a strong light emission in visible light wavelength range. As $R<6$ sccm, recombination of electrons and holes in a-Si quantum dots is the main mechanism of photo/electroluminescence for Si-rich SiN_x films, however, for photoluminescence, gap states' luminescence is also in competition; as $R>6$ sccm, light emission of the SiN_x film originates from defect states in its band gap.
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1. Introduction

Light emission from Si-based materials is an important research area for potential optoelectronic applications compatible with nowadays very large scale integrated silicon technology. As a rather low electron–hole pair recombination rate due to an indirect band gap, bulk Si is known to be inefficient in light emission. Since Si nanostructure has been believed to be responsible for the visible light emission in porous Si, discovered by L. T. Canham et al. [1], various techniques have been attempted to fabricate Si nanostructure in a host matrix of SiO_x. However, post annealing at temperatures over 1100 °C is required for the formation and crystallization of silicon nanoparticles in SiO_x to get a high efficiency photoluminescence (PL) [2,3]. Recent researches [4,5] have showed that it is difficult to obtain visible luminescence from Si-rich SiO_x due to silicon–oxygen double bonds, even with sufficiently strong quantum confinement effect in the nm-sized nc-Si. On the other hand, some experiments [6,7] with nitride surface passivation for nc-Si in SiN_x have been carried out, and shown that the light emission peaks are similar to that of SiO_x, centering in the near-infrared range of 700–900 nm.

However, recent researches show that high efficiency PL may arise from amorphous well-passivated silicon nanoparticles in SiN_x matrix. N. M. Park et al. [8,9] have observed a strong tunable luminescence from red to blue PL by controlling the size of amorphous silicon quantum dot embedded in SiN_x matrix deposited by plasma enhanced chemical vapor deposition (PECVD). Y. Q. Wang et al. [10–13] have prepared the same alloys by PECVD from SiH_4 and N_2 to get a PL center energy tunable from 2.0 to 2.9 eV, dependent on the silicon nanoparticle size. The origin of PL from a-SiN_x may arise from some causes, for example, radiative recombination through a quasidirect energy level as a result of the quantum energy in Si small clusters,

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recombination through the level between states in the band gap. It is still a matter of debate. V. A. Gritsenko et al. [14] explained the visible PL near the UV region in a-SiN_x thin films by the spatial variation of chemical composition in SiN_x. L. Zhang et al. [15] have reported that light emission in single-crystalline a-Si_3N_4 nanobelts is due to the intrinsic and defect energy levels. Despite of the controversy, the abovementioned investigations may indicate that amorphous nanoclusters are not necessarily bad light emitters. Furthermore, silicon nitride, rather than oxide, is a good matrix material due to its low band gap for tunneling of electrons and holes. More recently, K. S. Cho et al. [16] have fabricated light-emitting diodes using n-type SiC/SiN_x/p-type Si heterojunction and high efficient visible electroluminescence at 2.4 eV has been observed. L. Y. Chen et al. [17] and Z. Pei et al. [18] have also observed visible electroluminescence from silicon nanocrystals embedded in amorphous silicon nitride matrix.

In this paper, we report a study on the plasma process and the structural evolution and luminescence properties of amorphous hydrogenated silicon nitride films. a-SiN_x films were deposited from SiH_4 (80% Ar diluted) and using the microwave electron cyclotron resonance chemical vapor deposition (ECRCVD) method under variable NH_3 gas flow rate with microwave input power of 600 W and pressure of 0.5 Pa. Optical emission spectroscopy (OES) was used to study the discharge environment in the variable SiH_4+Ar:NH_3 flow ratio. The influence of the NH_3 gas flow rate on the growth and structural properties of ECR deposited a-SiN_x films, and correlations between their structures and photoluminescence (PL)/electroluminescence (EL) were analyzed in detail.

2. Experiments

The a-SiN_x films were deposited by the microwave ECRCVD technique. Microwave with a frequency of 2.45 GHz was introduced into the plasma via a waveguide. The magnetic field with a magnitude of 0.0875 T required for electron cyclotron resonance was excited through a group of excitation coils. The flow rate of SiH_4+Ar was fixed at 20 sccm, while NH_3 flow rate was varied between 2 and 13 sccm. NH_3 gas was injected upstream to the ECR region while the diluted SiH_4 was introduced downstream through a gas dispersion ring. For all the processes of film deposition, the microwave input power and the total pressure were kept at 600 W and 0.5 Pa, respectively. In the microwave ECR plasma, electron absorbs the microwave energy through cyclotron resonance and collides with the parent gases causing their breakdown into a large number of species, and electrons and ions are present in the plasma environment. In a SiH_4+NH_3 plasma, the relative concentrations of these species, such as H, SiH, NH, etc., were measured with OES. The thickness of a-SiN_x films was measured with ET350 profilometer. The infrared absorption spectrum of a-SiN_x films on KBr wafer was measured with a Jasco IR-670 spectrometer. X-ray photoelectron spectroscopy (Kratos XSAM-800) with monochromatic Al K_α ($h\nu$=1486.6 eV) was used to determine the elemental composition and chemical bonding states of a-SiN_x films. Ion sputtering was carried out with 2.5 keV Ar^+ beam at an incident angle of 45° to the normal sample surface for 3 min prior to the sample detection. The scanned area was 3 mm × 3 mm with the analyzed one of 10 μm × 10 μm. The PL at room temperature was excited with 350 nm from a Xe lamp and PL or EL was measured on a Jasco FP-6500 fluorescence spectrometer. The EL device for a-SiN_x film was fabricated as follows, silicon nitride film with variable NH_3 flow rate R and the thickness of about 80 nm was deposited on the indium–tin–oxide (ITO)/glass substrate, which was employed as an anode, high purity silver paint as a cathode was dotted on the film surface and ITO by forming Ohmic contacts, two copper wires with a diameter of 0.1 mm connected them separately, and then the whole device was put into the vacuum chamber for pumping and drying.

3. Results and discussion

3.1. Plasma properties and films deposition rate as a function of gas flow ratio

Some of the species that are expected to play important roles in the film deposition were easily observed via optical emission spectroscopy in the ECR discharge. Fig. 1 shows a typical optical emission spectrum in the ECR plasma with [SiH_4+Ar]:[NH_3]=20 sccm:10 sccm. The intensities of the characteristic peaks at 251.3 nm and 287.9 nm due to Si radical and 336.0 nm due to NH radical, which are believed to contribute to the film deposition, were chosen for monitoring these species in the plasma. Atomic H_α and H_β, located at 655.9 nm and 485.7 nm, and some other peaks with low intensities, such as NH at 357.7 nm and 385.8 nm, Ar around 419.5 nm, are also indicated in this figure. Formation of the above species depends strongly on the high-energy tail of the electron energy distribution function in the ECR plasma. In the SiH_4 RF glow discharge, SiH, SiH_2 species, typically at 414.2 nm and 577 nm [19,20], appears with a moderate intensity, however, it is not present in our experiment, this may arise from the high density ECR plasma with the electron concentration more than 10^{11} cm^{-3}, causing smaller fragment of radicals due to electron–radical or metastable Ar–radical collision in comparison with that in the RF glow discharge.

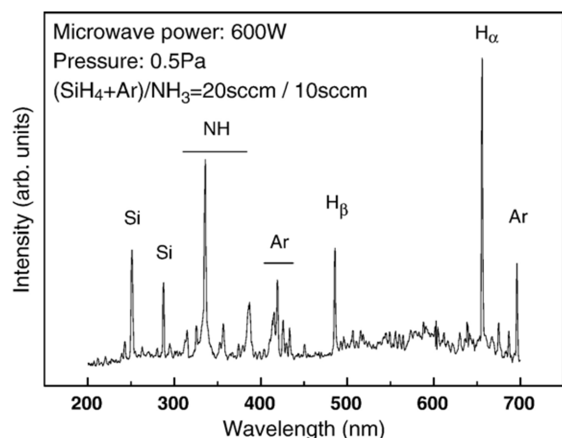

Fig. 1. Typical emission spectrum of a-SiN_x sample.

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