# NANOCRYSTALLINE $SiC_xN_y$ FILMS: RPECVD SYNTHESIS AND TRANSFORMATION UNDER THERMAL ANNEALING

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The $SiC_xN_y$ compound has attracted increasing attention because it is expected to combine properties of $Si_3N_4$, $C_3N_4$, SiC. It is suggested that promising features of silicon carbonitride would be due to the chemical bonding of Si, C, N atoms in ternary compound.

The silicon carbonitride films were synthesized by RPECVD at total pressure of $6\times10^{-2}$ Torr in the temperature region of 473-1173K using mixture of helium, ammonia and hexamethyldisilazane as a volatile single-source precursor. The synthesis of $SiC_xN_y$ films in system containing ammonia was carried out at different $P_{NH3}/P_{HMDS}$ ratios, namely: 0.3, 0.73, 1.6 and 2.1. Helium was used as an activator of gaseous species in plasma enhanced processes. The substrates were (100)Si, (100)GaAs wafers and fused silica slides. Silicon carbonitride films were heated up to 1123 K at pressure of helium of $10^{-2}$ Torr during two hours. Different techniques such as IR, Raman spectroscopy, ellipsometry, XPS, SEM, HREM, SAED, XRD using synchrotron radiation and electrophysical measurements were used to study the physical and chemical properties of $SiC_xN_y$ films.

The $SiC_xN_y$ films synthesized in (HMDS+He) and (HMDS+$NH_3$+He) systems are uniform, nonporous and their surface micromorphology has no peculiarities. The films exhibited very high optical transmittance (~ 70-90 % for λ=600-700 nm), characteristic for wide band gap materials. The films had thicknesses of 200÷4000 nm in dependence on growth conditions. The observed refractive index values were 1.7 - 3.2 and 1.5 - 2.4 for gaseous mixtures (HMDS+He) and (HMDS+$NH_3$+He), correspondingly. The rise of the growth temperature leads to the increase of refractive index values of the $SiC_xN_y$ films. The refractive index values decrease with the $P_{NH3}/P_{HMDS}$ ratios rise. It is probably due to an increase of Si-N bond concentration in these films.

IR-spectra of silicon carbonitride films synthesized in the temperature region of 473-1173 K and in two systems consist of the main adsorption band of 650-1200 $cm^{-1}$, corresponding to the superposition of the Si-C (800 $cm^{-1}$), the Si-N (900-950 $cm^{-1}$) and the C-N (~1030 $cm^{-1}$) stretching modes. There are no hydrogenous bands in the spectra. The band of 650-1200 $cm^{-1}$ was deconvoluted using Gaussian line shapes into the Si-C (800 $cm^{-1}$) and Si-N (950 $cm^{-1}$) bands. the rise of the temperature up to 1123 K leads to the monotonic increasing of the integral intensity ratio ($I_{Si-C}/I_{Si-N}$ ) in IR-spectra of films grown from (HMDS+He) mixture. Opposite the rise of ammonia concentration and the growth temperature leads to increase of concentration of Si-N bonds in films grown in (HMDS+$NH_3$+He) system.

Raman measurements showed that the films grown in both systems contains the wide bands in the region of 700-980 and 1200 - 1600 $cm^{-1}$. The first band can be assigned to Si-C, Si-N and 2 LO of the silicon substrate whereas the second asymmetric band is very similar to that of nanocrystalline or amorphous carbon with two broad bands centred at around 1360 $cm^{-1}$ and 1540 $cm^{-1}$ D and G bands of disordered $sp^2$ carbon. As follows from the integral intensity ratios of the D and the G bands ($I_D/I_G$), the rise of temperature leads to the decrease of the intensity and width of the D band, but the increase of ammonia concentration leads to an increase of the D band intensity.

According to XPS study the concentration of the main elements changes insignificantly with the growth temperature rise. The Si 2*p* photo electron peak could be resolved into three components, centred at 99.2 (Si-Si), 101.5 (Si-C) and 102.8 eV (Si-N). In the case of ammonia system, component centred at 99.2 eV (Si-Si), disappears whereas components belonging to Si-C and Si-N bonding shift up to 101.8 and 103.1 eV, respectively. The XPS spectrum for C 1*s* of $SiC_xN_y$ films grown without ammonia consists of three components, centred at 283.7 (C-Si), 284.7 (C-C) and 285.7 eV (C-N). In system with ammonia these components also shift and have following values: 283.8, 285.1 and 287.2 eV, respectively. The XPS spectrum belonging to the N 1s consists of one component, centred at 397.5 eV (N-Si) in case of films grown in (HMDS+He) system. Opposite the N 1*s* peak consists two components centred at 397.8 (N-Si) and 399.7 eV (N-C) in case of films grown with ammonia addition.

XRD patterns of $SiC_xN_y$ film shows that the peaks' position is close to α-$Si_3N_4$ phase. There are some unknown peaks at small diffraction angles which do not correspond to peaks of known phases of the Si-C-N system, such as SiC, $Si_3N_4$ and C (graphite). All silicon carbonitride films contain carbon atoms which are scarcely affected on the modification of the lattice parameters of α-$Si_3N_4$, due to the similar atomic radius of carbon and silicon. The crystal size was estimated by broadening of the diffraction peak using known Debye - Scherrer formula. The approximate size of nanocrystals was found to be equal to 2÷7 nm depending on the growth temperatures. HREM and SAED data were shown that $SiC_xN_y$ films grown in (HMDS+He) system present a distribution of spherical nanocrystals with diameter about 2 nm in amorphous matrix. The addition of ammonia to initial mixture leads to the formation of amorphous films with embed nanocrystals with less size.

The variation of initial gaseous mixture allows synthesizing the gradient films based on silicon carbonitride.

C-V and I-V measurements showed that $SiC_xN_y$ films obtained under different growth conditions can be dielectrics of wide spectra of application: from high-K up to low-K materials. The thermal annealing of $SiC_xN_y$ films leads to densifying, ordering of structure and increase of nanocrystals size.

The thermal annealing of $SiC_xN_y$ films leads to increase of their transparency, densifying, ordering of structure and increase of nanocrystals' size.

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