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Low-*k* dielectrics on base of silicon carbon nitride films

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Abstract

Thin silicon carbonitride films were synthesized by PECVD using siliconorganic compound as single-source precursor within a temperature range of 373–623 K. IR and Raman spectroscopy, AES, XPS, ellipsometry, XRD using the synchrotron radiation, EDS, SEM, AFM, measurements of electrophysical, mechanical characteristics and optical properties were applied to study their physicochemical and functional properties. It was shown that low temperature films are low-*k* dielectrics with the following characteristics: a dielectric constant of 3.0–7.0, specific resistance, $\rho = 10^{13}–10^{16}$ Om × cm, $E_{\text{dielectric breakdown}} \sim 1$ MV/cm, surface state density $N_{ss} \sim 2.4 \cdot 10^{11}$ cm$^{-2} \cdot$eV^{-1} and fixed charge density of about 1.6×10^{11} cm^{-2}. The bandgap of the films changes from 5.35 up to ~3.30 eV. Obtained films are very flat and smooth, root mean square roughness R_{ms} equals to ~0.5–1.0 nm. Microhardness of these films changes from 1.9 up to 2.4 GPa, and Young's modulus changes from 12.2 up to 15.9 GPa.

Keywords: Silicon carbonitride films; Low-*k* dielectrics; PECVD; Electrophysical characteristics; Optical properties

1. Introduction

The increasing need for faster integrated circuits has resulted in the realization of higher-speed and higher-density semiconductor devices. However, further decrease of feature sizes to value lower than 1 μm has introduced certain limitations such as the interconnection delay which, namely, is the resistance–capacitance delay. The introduction of Cu and low-*k* dielectrics has incrementally improved the situation as compared to the conventional Al/SiO_2 technology by reducing both resistivity and capacitance between wires.

Generally speaking, a low-*k* material is an insulating material that exhibits weak polarizability when subjected to an externally applied electric field. The relative permittivity of materials is smaller if materials do not contain polar molecules and involve pores. Decreasing the dielectric constant, however, causes deterioration in mechanical strength and long-term reliability — a significant drawback for practical application of low-*k* materials.

Among various candidates for low-*k* materials with a dielectric constant of 2.0–3.0, Si–C–N films are very promising because of their low dielectric constant and high hardness, and other excellent functional properties, such as superplasticity, a high strength, enhanced oxidation, corrosion resistance and Cu diffusion protection.

Currently, silicon carbonitride films have been produced with ion sputtering deposition of carbon and silicon in nitrogen atmosphere, N^+ implantation into SiC surface, laser vapor phase reaction of hexamethyldisilazane (HMDS) $Si_2NH(CH_3)_6$ with ammonia, chemical vapor deposition (CVD) and plasma enhanced CVD using $Si(CH_3)_4–NH_3–H_2$, $SiH_4–NH_3(N_2)–CH_4$ (or N_2H_4)–H_2(Ar), $SiCl_4 + NH_3 + C_3H_8 + H_2$, as initial atmospheres [1–4]. HMDS is the most important single-source precursor for preparation low-*k* dielectrics on base of SiC_xN_y due to the molecules of HMDS contain ready fragments with less polarizable bonds such as Si–C, C–C, Si–CH_3, C–H.

The goal of our research is to develop low temperature method of obtaining of SiC_xN_y films with low permittivity, to study their physicochemical, and electrophysical properties, and to determine the relationship between properties, chemical composition and chemical bonding.

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2. Experimental

The low temperature synthesis of SiC_xN_y films with the wide interval of x and y was carried out by remote plasma enhanced decomposition of HMDS as single-source precursor using gaseous mixtures: (HMDS + He), (HMDS + N_2) in the temperature range of 373–623 K, in r. f. power range of 15–40 W and total pressure in reactor of $(4–6)\times10^{-2}$ Torr [5,6]. Wafers of Si (100) and fused silica were used as substrates. The effect of the growth temperature, chemical composition of the initial gas phase, r.f. plasma power, total pressure in the reactor on the certain electrophysical characteristics, microstructure, chemical and phase composition of the films was studied. The influence of chemical composition on the physical and chemical properties of the silicon carbonitride films was investigated using a complex of the following modern methods: FTIR and Raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), microhardness and Young modulus determination by nano-indenter, electrophysical (I–V and C–V) measurements, optical measurements, ellipsometry. X-ray diffraction using synchrotron radiation (XRD–SR) measurements were carried out at the station «Anomalous scattering» of the Siberian Center of Synchrotron Radiation (BINP SB RAS).

The thickness and refractive index of the all films were measured by means of an ellipsometer model LEF-3 at the wavelength of 632.8 nm. The measurements were carried out at seven angles. FTIR absorption spectra of the films were recorded in a transmission mode on FTIR SCIMITAR FTS 2000 spectrometer with range 300–4000 cm^{-1}. 32 scans and the aperture equal 4 at achievable resolution 2 cm^{-1} were used during the measurements. Raman measurements were carried out by PHILIPS PU-95 and Triplemate, Spex spectrophotometer.

The X-ray photoemission spectra were obtained by MAC-2 (RIBER) analyzer using non-monochromatic Al K_α radiation (1486.6 eV) with the power of 300 W and X-ray beam diameter about of ~5 mm. The energy resolution of the instrument was chosen to be 0.7 eV, so as to have sufficiently small broadening of natural core level lines at a reasonable signal-noise ratio. Under these conditions the observed full width at half maximum (FWHM) of the Au 4f7/2 line was 1.31 eV. The binding energy scale was calibrated in reference to the Cu 3p3/2 (75.1 eV) and Cu 2p3/2 (932.7 eV) lines, assuring the accuracy of ±0.1 eV in any peak energy position determination. Since the SiC_xN_y are good dielectric films, the photoelectron energy drift due to charging effects was taken into account in reference to the position of C 1 s (284.6 eV) line generated by adventitious carbon on the sample surface as inserted into the vacuum chamber. The component of adventitious carbon was derived from complex carbon peak structure by means deconvolution. This subpeak have always presented in spectra though the precleaning procedure which consists in treatment by hot isopropyl alcohol, then etching in diluted solution of HF acid (1HF: 20H_2O) and finish treatment by hot isopropyl alcohol. This treatment is soft and less selective in contrast to etching by Ar^+ ion bombardment.

The micromorphology of surface was studied by scanning electron microscope (model JEOL JSM 6700F) supplied the apparatus for element composition determination by energy dispersive spectroscopy (EDS). Surface morphology and roughness of the films were examined by AFM using microscope model Solver PRO-M-NT-MDT. The measurements were performed at room temperature in air using V-shaped silicon cantilevers with a tip radius curvature of 10 nm.

3. Results and discussion

3.1. Ellipsometry

The SiC_xN_y films had thicknesses from 200 to 3000 nm depending on growth conditions. The rise of the growth temperature and r. f. power leads to the increase of refractive index values of the SiC_xN_y films grown in (HMDS + He) and (HMDS + N_2) gaseous mixtures. The refractive index values of SiC_xN_y films having low values of permittivity vary from ~1.5 up to ~2.0.

3.2. IR spectroscopy

Important information concerning the chemical bond types existing in low temperature SiC_xN_y films was obtained by the FTIR spectroscopy study depending on r. f. power. According to these data, a wide band of 450–1350 cm^{-1} is observed in the spectra of films grown from (HMDS + He) gaseous mixture at 15 W (Fig. 1a–b). In contrast to high temperature films [7] there are hydrogenous bonds such as deformation stretching vibration of Si–CH_3 bonds at 1250 cm^{-1}, stretching vibration C–N or Si–CH_2–Si bonds at ~1400 cm^{-1}, stretching vibration of Si–H or N=C=N bonds at 2100–2200 cm^{-1}, asymmetric stretching vibration of C–H bonds at 2900 cm^{-1}, vibration of N–H at 3390 cm^{-1} (Fig. 1a) [8]. The main wide IR peak was approximated by sum Gaussian curves and their integral intensities were calculated. This analysis showed that the main IR adsorption band mostly corresponds to the superposition of asymmetric stretching vibration of N–Si–N bonds at 450 cm^{-1}, symmetric stretching vibration of Si–N bonds at 950 cm^{-1}, stretching vibration of Si–C bonds at 800 cm^{-1}, and stretching vibration of Si–O or C–N bond at 1030 cm^{-1}. The increase of r.f. plasma power up to 40 W leads to the decrease of intensities or the disappearance of the IR bands relating to hydrogenous bonds. This influence into chemical composition is to a greater extent then an increase of growth temperature (Fig. 1b–d). The using of (HMDS + N_2) gaseous mixture at similar T_{growth} and r.f. power leads to the decrease of integral intensity of S–C bond and increase of integral intensity of Si–N bond in SiC_xN_y films.

3.3. Raman spectroscopy

It was observed that Raman spectra of silicon carbonitride films grown at low temperatures and any r.f. power represent continuous spectrum, separate peaks are absent. Lack of specific Raman spectrum with two broad bands centred at