Surface & Coatings Technology 205 (2011) S214–S217

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Structural and optical properties of a-SiCN thin film synthesised in a microwave plasma at constant temperature and different flow of CH_4 added to HMDSN/N_2/Ar mixture

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ARTICLE INFO

Article history:
Received 10 September 2010
Accepted in revised form 6 February 2011
Available online 13 February 2011

Keywords:
Microwave plasma assisted chemical vapour deposition
SiCN
Chemical composition
Optical properties
Hexamethyldisilazane

ABSTRACT

Amorphous SiCN (a-SiCN) thin films were deposited by microwave plasma assisted chemical vapour deposition (MPACVD) using N_2, Ar, CH_4 and vaporised hexamethyldisilazane (HMDSN) gases. The CH_4 ratio (0 to 12%) effect on composition, structural and optical properties of thin layers synthesised at a constant growth temperature of 550 °C has been studied. It was found that layers are mainly composed of silicon nitride like compound and that CH_4 addition leads to denser and smoother films. An augmentation of the refractive index from 1.72 to 2.05 and Tauc gap from 4.3 to 4.7 eV has also been measured with CH_4 ratio increase from 0 to 12%. These results show that CH_4 addition to the feed gas allows varying the composition, morphology and the optical properties of HMDSN a-SiCN based films.

1. Introduction

Silicon carbonitride thin films exhibit superior features such as high hardness [1,2], low friction coefficient [1,3], high resistance to oxidation [4,5], chemical inertness [6,7] and wide band gap [8–10]. One of the most attractive characteristic of this ternary material is the wide range of stoichiometries of a-SiC_xN_y which depends on experimental deposition conditions [11,12]. It is thus possible to synthesise material between SiC and Si_3N_4 whose band gap value rises from 2.3 to 5 eV respectively. Refractive index as well can be changed on a large scale depending on atomic composition and thin film morphology [11,12]. The possibility of tuning electronic and optical properties of this material make it promising for optoelectronic applications. SiCN materials were already found to have various potential applications such as UV detector [13,14], low wavelength emitting diode [15,16] and antireflection coatings or passivation layers for solar cells applications [17,18]. Whereas silane (SiH_4) is widely used in MPACVD processes for silicon carbonitride thin films synthesis, this gas is extremely pyrophoric. Therefore, organosilicon compounds which are much easier to handle appear very promising for SiCN thin film deposition. However, the process is much more difficult to control due to their complex structure and the plasma chemistry needs further study. In the present work, harmless hexamethyldisilazane (HMDSN: $(CH_3)_3$–Si–NH–Si–$(CH_3)_3$) is used as a precursor. Among organosilicon compounds, HMDSN is interesting for SiC_xN_y:H deposition because it contains Si–C and Si–N bonding and it has already shown its ability for silicon carbonitride film forming [19–21].

In this work, the impact of CH_4 ratio on thin film structure, composition and optical constants was determined for a fixed growth temperature of 550 °C. In addition, plasma diagnostics such as optical emission spectroscopy (OES) and in-situ Fourier Transform Infrared Spectroscopy (FTIR) were used in order to provide information about the chemistry of the plasma.

2. Experimental

All films were deposited during 1 h in a resonant MPACVD system [22] with a gas mixture of N_2, CH_4, Ar and electronic grade HMDSN vapour. Flow of 0.5 sccm of gaseous HMDSN was introduced continuously into the reactor along with Ar carrier gas at a flow rate of 15 sccm. CH_4 flow was varied in the range 0 to 8 sccm, corresponding to ratio from 0 to 12%. In the following, plasmas and films characteristics were observed as a function of CH_4 ratio which refers to this experimental deposition parameter. N_2 gas flow rate was adjusted to keep a constant total flow rate of 65 sccm for all experiments. Microwave power was chosen at 600 W and deposition pressure at 25 mbar. Si (100) wafer and fused silica pieces were used as substrates. Prior to introduction in the reactor, the samples were cleaned according to the protocol described in [22]. In order to keep a

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doi:10.1016/j.surfcoat.2011.02.014

constant substrate temperature, a heater is used to keep the substrates at a temperature of 550 °C, whatever the CH_4 rate. This temperature is chosen because substrate holder temperature in a CH_4/N_2/Ar/HMDSN plasma is affected by CH_4 ratio. An increase of CH_4 flow rate leads to a substrate temperature increase from 240 °C (0% CH_4) to 520 °C (9% CH_4) most likely because the plasma moves closer to the substrate. The combined effect of CH_4 ratio and growth temperature increase has been studied previously [21].

During the process, OES was achieved with an Andor Mechelle spectrometer in order to study the behaviour of emitting species from the plasma. Fourier Transform Infrared (FTIR) BRUKER EQUINOX 55 spectrometer in the range 400–4000 cm^{-1} in the transmitting mode was used to monitor IR gas absorbing species.

Thin films roughness was measured by means of atomic force microscopy using a Dimension 3100 Scanning Probe Microscope in tapping mode with Silicon cantilevers. Atomic composition and bonding states of the a-SiCN thin layers surface were studied by a Kratos XPS Axis-Ultra with Al K_α (1486.6 eV) excitation. FTIR analyses were performed in transmission mode within 15 min after deposition by the same FTIR spectrometer in the range 500–5000 cm^{-1}. Absorbance was normalised to the film thickness measured from cross view scanning electron micrographs of deposited layer.

Optical properties of SiC_xN_y:H layers are determined by UV–Visible transmission measurements of samples grown on fused silica substrates using a Varian Cary 5000 spectrophotometer in the range 200–3000 nm. The optical parameters (the refractive index n, the extinction coefficient k and the Tauc gap E_g) were deduced by fitting a theoretical transmittance model to experimental data according to Swanepoel's work [23]. E_g is obtained using, in the strong absorption zone of the spectra, the Tauc expression of absorbance in the theoretical model: $\alpha E = B(E - Eg)^2$ with α the absorption coefficient (cm^{-1}), B the Tauc coefficient ($cm^{-1}\,eV^{-1}$), and E the energy of incident wavelength (eV).

3. Results and discussion

The addition of CH_4 to the feed gas increases carbon and hydrogen amount in the plasma. This can be observed by the enhancement of the emitted light from carbonaceous and hydrogenated species in OES measurements. A maximum of emission is obtained at 6% CH_4 for Si (288.1 nm), CH (431 nm), NH (336 nm), C_2 (516 nm) and N_2 second positive (337 nm) (not presented here). CN (B) (388 nm) is the most emitting specie from the plasma and a saturation of this line is obtained for 6% CH_4 (cf. Fig. 1). FTIR in situ spectroscopy analysis points out that the efficient dissociation of HMDSN and CH_4. Indeed, the absorption signal corresponding to these reactants are decreased by more than 90% since the plasma is on. It also reveals the production of HCN (713 cm^{-1}) and C_2H_2 (730 cm^{-1}). HCN density linearly increases with CH_4 ratio (cf. Fig. 1). According to these results, an important part of the added carbon with CH_4 addition reacts to form CN and/or HCN.

Fig. 2 exhibits the growth rate and the rms roughness as a function of the CH_4 ratio. The addition of 6% of CH_4 to the N_2/Ar/HMDSN plasma leads to a decrease of the thickness growth rate of about 40% and of the rms roughness of 80% compared to the film obtained in N_2/Ar/HMDSN plasma. Insets in Fig. 2 of SEM cross view micrographs of films deposited for 0 and 6% of CH_4 show the important structure modification induced by CH_4 addition. Thin film obtained in N_2/Ar/HMDSN plasma exhibits a loose structure with well defined particle boundaries whereas the one synthesised in plasma with 6% CH_4 seems compact. CH_4 addition induced denser and smoother films. Whatever the CH_4 ratio, the thin films are amorphous which is an expected result considering the relatively low growth temperature as noticed elsewhere [10].

3.1. Composition

The atomic composition from XPS measurements reveals (cf. Fig. 3) that thin films contain mainly nitrogen and silicon, whatever the CH_4 ratio. An important decrease of oxygen content from 20% to about 5% occurs when CH_4 is introduced in the gaseous mixture. Because oxygen content is highly correlated to thin film roughness, we assume that oxygen comes mainly from thin film oxidation after air exposure. The carbon content augments from 8 to a maximum of 16% for CH_4 ratio varying from 0 to 3%, and then it remains constant at this value up to 9% of CH_4 and decreases slightly. Nitrogen and silicon content do not vary significantly and remain at a high value of about 35–40% for all the films.

Decompositions of the N1s, C1s and Si2p XPS peaks highlight that the major part of N atoms is bonded to Si since the N1s XPS peak can only be decomposed into one peak centred at 397.4 eV. N and Si XPS decomposition peaks show unambiguously that thin films are mainly composed of SiN_x. C–Si bonds (283 eV) are only quantified at a few percent and do not exceed 5% of the total bonding whatever the CH_4 ratio. A slight C–Si bonds increase can be noticed when CH_4 ratio rises from 0 to 12% (cf. Fig. 4). However C–C and/or C–H bonds (284.5–284.7 eV) remain the most important carbon binding.

FTIR measurements point out that films are mainly composed of amorphous hydrogenated silicon nitride. The IR absorption spectra are composed of three main areas as shown by Fig. 5. The major IR absorption peak lies between 400 and 1400 cm^{-1} and mainly corresponds to Si–N asymmetric stretching vibration centred around 850–870 cm^{-1} (cf. Fig. 6). Most probable additional vibrations contributing to this peak are Si–C (790–820 cm^{-1}), Si–O around

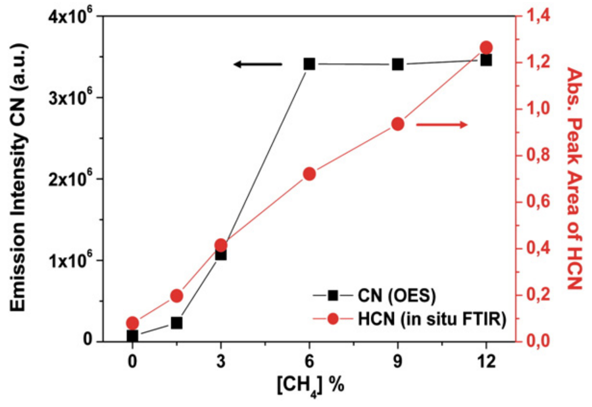

Fig. 1. Emission intensity of CN(B) at 388 nm and FTIR HCN area at 713 cm^{-1} as a function of CH_4 ratio.

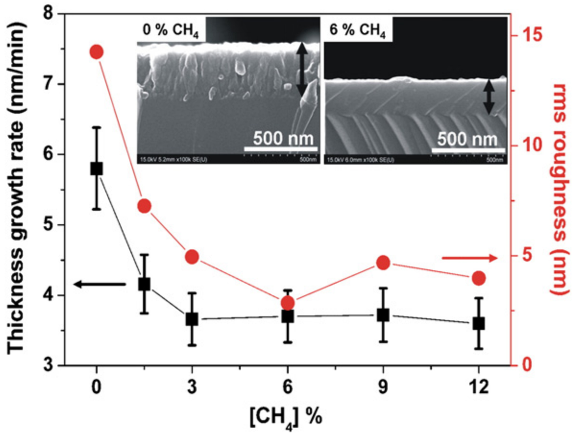

Fig. 2. Deposition rate and rms roughness of a-SiCN thin films as a function of CH_4 ratio. Insets show SEM micrographs cross view of thin films obtained for 0 and 6% of CH_4.