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CHARACTERIZATION OF PLASMA DEPOSITED CARBON-SILICON OXIDE THIN FILMS

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Abstract. An experimental study of plasma enhanced chemical vapor deposition technique is presented. Low-pressure radiofrequency inductive plasma discharges of argon, oxygen and hexamethyldisiloxane are employed to deposit silicon oxycarbide thin films. The effect of working gas mixture, total processing pressure and deposition time on film composition has been investigated. The characterization of deposits is performed by means of Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR), Electron Paramagnetic Resonance (EPR), Raman spectroscopy and Scanning Electron Microscopy (SEM).

1. INTRODUCTION

Silicon-based thin films and nanostructures hold great interest for applications as diverse as microelectronics, photonics, MEMS and catalysis (see Stabler et al. 2018). The development of materials gifted with satisfactory characteristics, such as controlled chemistry and morphology, can benefit a variety of applications. Plasma sources are of great interest in industrial applications and processing technology; in particular, inductively coupled plasma (ICP) discharges are one of the most efficient yet cost effective way to produce dense plasma by low power input and are also able to process both conducting and dielectric materials (see Conrads et al. 2000).
This paper wants to illustrate an instance for the deposition of carbon-containing silicon thin films employing Plasma Enhanced Chemical Vapour Deposition (PECVD)

and a comprehensive characterization of the deposited materials, for the purpose of understanding how plasma parameters influence the growth processes.

2. EXPERIMENTAL SET-UP

The PECVD reactor configuration is displayed in Figure 1. The deposition chamber is a cubic box with 40 cm per side and the vessel is connected to the main pumping line, composed by a rotary and a turbomolecular pump in series. The plasma source is placed inside a cap on the top of the chamber. It is an ICP commercial antenna by CCR Technologies Gmbh, it is composed of a 65 x 2.5 mm strip electrode cylindrically bent with a 17 cm diameter. The antenna is coupled to a RF 13.56 MHz power generator (Dressler RF Generator, Cesar 1310) through a manual matching box with two variable capacitors and equipped with a cooling water system. Approximately, the RF voltage as well as the current are uniformly distributed all along the antenna surface (see Weiler et al. 1998). A narrow injector inlets the gases for the plasma discharge directly above the antenna.

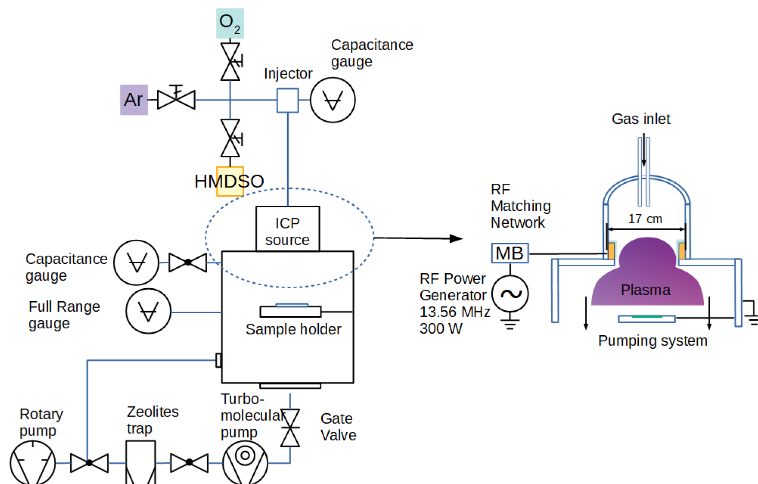

Figure 1: Schematic diagram of the deposition system and the ICP plasma source.

The vacuum vessel and the sample holder, and consequently the substrates, are grounded. In steady state operations, the RF generator supplies 300 W to the system, which it is the maximum allowed by the antenna heat dissipation system. The backward power is in the range of 10-15%, depending on the total pressure inside the chamber. A sheath is formed between the plasma and the sample holder and the sheath potential is 5-10 V lower than the plasma potential, while the electron temperature is 1-2 eV (see Barni et al. 2007).
The gas carriers of the discharge are argon and oxygen, and the precursor is hexamethyldisiloxane (HMDSO, Fulka ≥98%), a volatile organosilicon compound which, having a high vapour pressure (43 mbar at 20°C), easily evaporates and can sustain high flow rates under vacuum. The source gases are flowed through micrometer valves into the plasma chamber and partial pressures are monitored using a capacitance pressure gauge and a full range vacuum gauge. The partial pressures of the

ingoing gases determine the composition of the starting mixture for the deposition process, HMDSO has been varied from 10 to 40% of the total treatment pressure and the O_2:Ar ratio from 3:1 to 0:1. The estimated hydrodynamic conditions assure that the mixture is well-mixed in the flow direction. The depositions are performed varying the starting gas mixture, the total processing pressure ($3{\cdot}10^{-2}$-$3{\cdot}10^{-1}$ mbar) and deposition time (10-30 min). The substrate are Si(001) wafers, aluminium foils and alumina slabs, they are placed directly within the diffuse plasma region.
Post deposition thermal treatments are performed in order to allow desorption of interstitial species and induce crystallization of the amorphous layer. The films are annealed for 1h at 1050°C in controlled atmosphere, with a nitrogen flux of 8 L/min.

3. RESULT AND DISCUSSION

Operating parameters during deposition processes have been varied in order to evaluate the films composition and morphology. The substrates have been partially masked to measure the films thickness by means of a mechanical profilometer. The average deposition rate was about 20 nm/min, with the maximum being 72 nm/min at the highest pressure and precursor concentration considered.

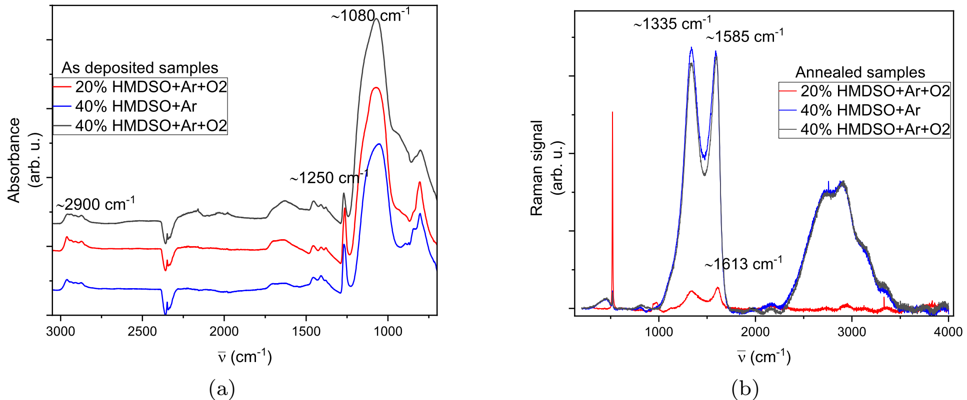

Figure 2: Normalized ATR-FTIR spectra in the 3050-700 cm^{-1} spectral region of the as-deposited films (a panel) and Raman spectra of the respective annealed samples irradiated at 514.5 nm (b panel).

ATR-FTIR spectroscopy in Figure 2(a) reveals several bonding arrangements in the as-deposited SiC_xO_y giving insight in their chemical structures (see Wavhal et al. 2006). The characteristic peaks of carbosilane and carbidic groups are present at 800 cm^{-1}. The strongest absorption band in the range 1000-1150 cm^{-1} is assigned to the asymmetric stretching vibrational modes of SiOSi and SiOC functional groups. Due to its broad structure, the deconvolution into Gaussian peaks of the absorption band and a study of the second derivative spectra are performed, the frequency shift of spectral components is attributed to changes in the SiOSi bonding angle. The $(CH_3)_3$Si-group is easily recognized by a sharp band at 1260 cm^{-1}. At higher wavenumbers, the typical stretching bands of sp^3 hydrogen coordinated carbon atoms in a linear aliphatic compound appear centred at 2900 cm^{-1}.

Electron Paramagnetic Resonance spectroscopy has been carried out in an X band ($\sim$ 9.4 GHz) spectrometer equipped with a high Q-factor cylindrical cavity (Bruker ER4122SHQ). The signal is unaffected upon sample rotation, it follows that the g-factor is isotropic. The experimental data are consistent with a g = 2.0055$\pm$0.0002, it is assigned to bulk silicon dangling bonds in $^{\bullet}$Si$\equiv$ Si configuration, called D center (see Pantelides 1986). The presence of amorphous silicon suggests the oxides deposits to have Si-rich domains. Annealing treatments are demonstrated to induce the phase separation between Si and the amorphous films (see Yi et al. 2002) leading to the segregation into silicon nanocrystals, whose size depends on the overabundance of Si atoms in the deposit. Post-annealing EPR measurements have confirmed the saturation of Si DBs, but still the optimal annealing conditions need to be met since further investigations do not confirm the presence of nanocrystals.
Micro-Raman spectroscopy has been employed to study the structural properties of SiC_xO_y annealed samples. In Figure 2(b) the spectra reveal a typical diamond-like-carbon structure confirming that graphite crystallites are formed (see Bokobza et al. 2014). The spectra display the characteristic G peak at 1582 cm^{-1}, corresponding to the LO phonon at Γ, and the defect-activated D and D' peaks at $\sim$1350 and $\sim$1620 cm^{-1}. The second-order of D peak, at higher wavenumber, suggests a great degree of disorder in the carbon structures. Data indicate that oxygen in the plasma mixture brings no significant differences in samples composition. The low wavenumber region of Raman spectra identifies silica or quartz components in the film, showing a broad and asymmetric band at 450 cm^{-1} assigned to SiOSi bending vibrations and its overtone at about 800 cm^{-1} (see Smit et al. 2003). The band deconvolution is not final in discerning the exact structure. It is possible to appreciate that in the 20% HMDSO+Ar+O_2 sample these bands are not present.
SEM images show that films are composed of quasi-spherical nanoparticles with the size in the range of 20 nm, determining a nodular surface which is a typical result of ballistic aggregation. At high total treatment pressure, mushroom-shaped extrinsic nodular defects begin to grow at the substrate interface.

4. CONCLUSION

The effect of working conditions on films composition has been investigated by means of different and complementary diagnostic techniques. Future approaches will be to develop electrical and optical plasma diagnostics to better understand the role of plasma parameters in deposition processes and devise an ad hoc post-deposition annealing to control crystallization. Additionally, new precursors will be tested.

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