Revista Brasileira de Aplicações de Vácuo, v. 26, n. 4, 193-197, 2007.

SYNTHESIS AND ETCHING OF AMORPHOUS SILICON CARBIDE THIN FILMS WITH HIGH CARBON CONTENT

M.A. Fraga[1*]; R.S. Pessoa[1]; M. Massi[1]; H.S. Maciel[1]; S.G. dos Santos Filho[2]; L.F. Bonetti[3]; L.V. Santos[3]
[1] *Laboratório de Plasmas e Processos , Instituto Tecnológico de Aeronáutica, São José dos Campos, SP, Brazil*
[2] *Laboratório de Sistemas Integráveis, Universidade de São Paulo, São Paulo, SP, Brazil*
[3] *Laboratório Associado de Sensores, Instituto Nacional de Pesquisas Espaciais, São José dos Campos, SP, Brazil*

Received: October 1, 2007; Accepted: December 9, 2007

Keywords: amorphous silicon carbide, PECVD, RIE, mass spectrometry.

ABSTRACT

Non-stoichiometric amorphous silicon carbide (a-Si_xC_y) thin films with high carbon content were synthesized on (100) silicon substrates in a PECVD system using SiH_4 and CH_4 as precursor gases. SiH_4/CH_4 flow ratio was adjusted by varying the SiH_4 flow rate and maintaining constant the CH_4 flow rate. RBS measurements show that the increase of the SiH_4 flow rate promotes a decrease of the carbon content in the film. To study the effect of carbon concentration on morphological and structural properties of the a-Si_xC_y films the following techniques were used: Atomic Force Microscopy (AFM), Raman Spectroscopy and Fourier Transform Infrared Spectrometry (FTIR). The etching process of these films was performed by reactive ion etching (RIE) using SF_6 as the reactive fluorinated gas and O_2 as an additive. In order to investigate the influence of O_2 concentration on etch rate of the films, a mass spectrometry system was connected to the RIE reactor.

1. INTRODUCTION

Silicon is not very suitable for applications that involve high temperatures, high voltage and aggressive gaseous environments. For these applications, silicon carbide (SiC) has attracted much attention because it exhibits excellent properties of strength, thermal and chemical stability, wide band-gap and high electron mobility [1, 2]. Despite these advantages, SiC technology is still at a research state, mainly because crystal growth is difficult to achieve, and partly because critical device fabrication techniques (etching, oxidation, for example) need to be improved. Nowadays, several methods are used to grow or etch SiC films. Relative to the film growth we can cite the molecular beam epitaxy (MBE), chemical vapor deposition (CVD), sputtering, plasma enhanced chemical vapor deposition (PECVD) technique [3], while for the etching process the techniques more usually used are standard reactive ion etching (RIE), inductively coupled plasma (ICP) or electron cyclotron reactor (ECR) [4, 5]. Amongst the most used deposition techniques, the PECVD process is very attractive due to its high deposition rate, low deposition temperature (< 400ºC), good adhesion and the ability to control the carbon content in the films [6-8]. However, at lower temperatures, PECVD SiC films are grown only in amorphous phase.

Recently, the application of a-SiC films in micro and optoelectronics devices has been subject of several studies and discussions in the scientific community [9, 10, 11]. A time that the optical and electronic properties of these films can be controlled by the changing the carbon and silicon content [8]. For instance, I. Pereyra and co-workers [7] showed that the gap optical increases with increases carbon content in the film.

Although some studies on properties of SiC films have been published, few works have investigated the growth and etching of non-stoichiometric *a-Si_xC_y* with high carbon concentration. Motivated by this, in this work we report the influence of the carbon concentration on characteristics of a-Si_xC_y thin films. For this, the SiH_4/CH_4 flow ratio was adjusted by varying SiH_4 flow rate for a fixed value of CH_4 flow rate. Morphology, chemical composition and structure of the a-Si_xC_y films were investigated by the following techniques: AFM, RBS, Raman spectroscopy and FTIR. Reactive ion etching (RIE) of the a-Si_xC_y films using SF_6/O_2 gas mixture has been performed for different oxygen concentrations: 20 and 80%. Moreover, the RIE system was connected to a mass spectrometer to allow a detailed study of the etching process in function of the carbon concentration in the a-Si_xC_y films and in function of the oxygen concentration in the SF_6/O_2 gas mixture.

2. EXPERIMENTAL PROCEDURE

a-Si_xC_y thin films have been produced on p-type (100) silicon substrate using a PECVD system equipped with a radio frequency (RF) source operated at a frequency of 13.56 MHz and power of 200W. The substrates were placed on a water cooled stainless steel cathode (6.5 cm in diameter) of a cylindrical chamber. During all depositions the following parameters were kept constant: substrate temperature (room temperature), pressure (200 mTorr), Ar flow rate (20 sccm), CH_4 flow rate (20 sccm) and deposition time (20 min.). In order to obtain a-Si_xC_y films with high carbon content the SiH_4 flow rate was varied from 1 to 4 sccm.

* mafraga@ita.br

After deposition, the thickness of each sample was measured using profilometry (TENCOR Alpha-Step 500 profilometer). The Raman analyses were performed at room temperature in the range of 400 to 2000 cm^{-1} with excitation provided by an argon laser operating at a wavelength of 514 nm. The RBS measurements were carried out using a 2MeV He^{+} beam and the RBS spectra were analyzed using a RUMP code (RBS spectroscopy analysis package) developed by Cornell University [12]. Infrared spectroscopy was performed by a Perkin Elmer spectrum 2000 Fourier transform infrared spectrometer in the range 400–4000cm^{-1}. A (100) silicon wafer was used as reference. AFM images were obtained by a SPM-9500J3 system in dynamic mode.
Plasma etching experiments were performed in a RIE parallel plate reactor using SF_6 as the reactive fluorinated gas and O_2 as an additive. During all etching studies the following parameters were kept constant: substrate temperature (20ºC), pressure (25 mTorr), rf power (50 W) and etching time (3 min.). To investigate the effect of the oxygen concentration on etch rate of the samples, the concentration was varied from 20% to 80% in the SF_6/O_2 gas mixture.
Etching rates are inferred by profilometry on the steps created on etched silicon substrates (cut out of the wafer with ~15×15 mm in size). To study the plasma etching medium, a mass spectrometry system (AccuQuad 200D – Kurt J. Lesker Company) was connected to the RIE reactor, to monitoring the variation of the main reaction products, CO, CO_2 and SiF_4. Details about the mass spectrometry analysis can be found in our previous work [13].

3. RESULTS AND DISCUSSION

3.1 DEPOSITION RATE

The thicknesses of the samples were measured by profilometry and RBS techniques. Fig. 1 shows that the deposition rate increases proportionally with the increase of SiH_4 flow rate in SiH_4 + CH_4 gas mixture. This behavior is correlated with the increase of the silicon concentration in the gas feed which results in an increase of the number of atoms incorporated in the film [14].

3.2 CHEMICAL AND STRUCTURAL PROPERTIES

RBS measurements were performed to determine the atomic composition of the a-Si_xC_y films. The concentration of species in the samples was calculated by means of computer simulations with the RUMP program. A convincing agreement between RBS and simulation data is observed (see Fig. 2).
In Table 1 the RBS results are summarized. It was observed that the increase of the SiH_4 flow rate promotes a decrease of the carbon content in film volume of until 68%. This carbon reduction is followed by the increase of the silicon concentration, promoting the formation of Si-C bonds. This fact is confirmed by the FTIR spectra of the a-Si_xC_y films showed in Fig. 3. All samples present a peak around ~790 cm^{-1} that corresponds to the Si-C bond. As can be observed, the intensity of this peak increases continuously with the increase of the SiH_4 flow rate.

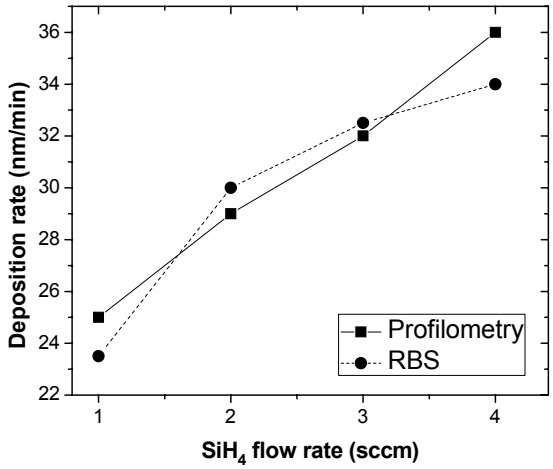

Fig. 1 - Deposition rate of a-Si_xC_y films as a function of the SiH_4 flow rate.

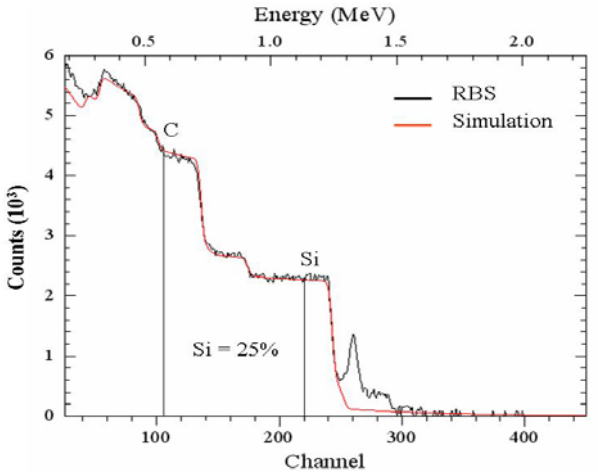

Fig. 2 - Typical RBS curve of the a-Si_xC_y film (for SiH_4 flow rate= 4 sccm).

Table 1 – Atomic concentrations of silicon, carbon and oxygen in the a-Si_xC_y films.

SiH_4 flow (sccm)	Si (at.%)	C (at.%)	O (at.%)
1	9.0	82.0	5.0
2	14.0	76.0	4.5
3	18.0	73.0	5.0
4	25.0	68.0	4.8

Also, in Table 1, it is possible to observe the presence of small amounts of oxygen for all analyzed films (~ 5%). The presence of this contaminant is also confirmed by FTIR spectra with one peak ~1040 cm^{-1} attributed to Si–O stretching vibration mode. The Si–O bond may be caused by the surface oxidization of the films.

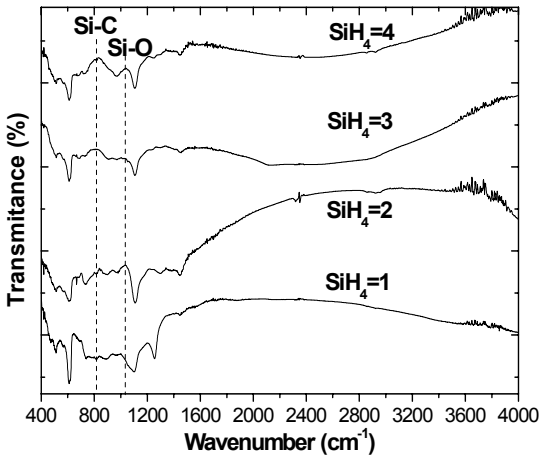

Fig. 3 – Infrared spectra of the a-Si_xC_y films.

In the characterization of crystalline SiC films, generally the Raman spectra contain the more interesting information because identify the Si–Si, Si–C and C–C bonds. As the films deposited in the present work are amorphous, the Raman spectra of these films do not exhibit peaks or bands corresponding to Si–C bonds (see Fig. 4). On the hand, the films deposited with 1 and 2 sccm of SiH_4 flow evidence peaks associated to C–C bonds at ~1340 cm^{-1} (D band) and ~1585 cm^{-1} (G band). Raman and FTIR spectra obtained in this work are similar to the reported by other authors for silicon-carbon alloys [15-16]. This proves that the films deposited are actually a compound of Si and C in amorphous phase.

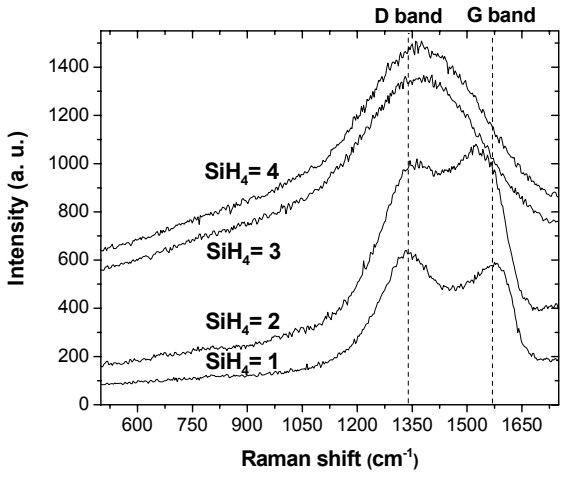

Fig. 4 - Raman analysis of the a-Si_xC_y films.

3.3 ETCHING STUDIES

Due to high bond energy between silicon and carbon, plasma assisted etching has been widely used to pattern the SiC [9]. Desired features in SiC etching include high etch rate, high anisotropy with no trench, and smooth surface with no residues. Thus, a detailed study on the influence of process parameters as RF power, total pressure and gas composition are important to obtain these requirements. In this work, a-Si_xC_y films have been etched in a RIE system at different O_2 concentrations in the SF_6/O_2 gas mixture: 20 and 80%O_2. The variation of O_2 concentration allowed evaluating the role of the carbon content in film and the influence of the oxygen addition gas on the etch rate and morphology of the etched material.

Fig. 5 shows the etching rate of the a-Si_xC_y films as a function of carbon content for different O_2 concentrations in the SF_6/O_2 gas mixture. As depicted, for both oxygen concentrations, the etch rate decreases with the increases of carbon content in a-Si_xC_y film. In contrast, Fig. 5 also shows the etch rate increases with the increases of the O_2 concentration from 20 to 80%. This occurrence is verified for all samples. As it is known, the addition of oxygen in fluorinated plasmas enables increase of the fluorite ion generation enhancing the etching of the silicon by the formation of SiF_4 volatile specie and also the etching of rich carbon layers by the formation of CO and CO_2 volatile species. However, according to literature, exists a limit where a high addition of O_2 starts to decrease the etching rate because the dilution of active chemical species [5, 13]. In SiC plasma etching investigations, the range between 20 – 60% O_2 concentrations was often demonstrated as the optimal mixture for getting the highest etch rate [5, 9]. But, in this work we verify that for 80% O_2 the etching rate still is raised. This result can be understood by the fact that the films described in the literature are stoichiometric. In our case, the films are non-stoichiometric and possess high carbon content.

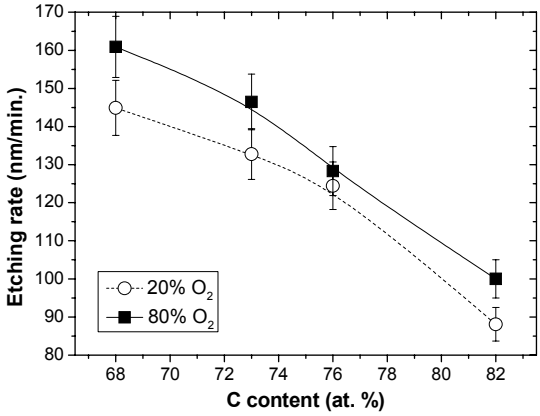

Fig. 5 – Etching rate of the a-Si_xC_y films as a function of carbon content for different O_2 concentrations in SF_6/O_2 gas mixture.

Still on Fig. 5, it is important to point out on the high values of etching rate obtained (up to 160 nm/min.). These results, when compared with the results of a crystalline film (around 35 nm/min. for films with approx. 68% carbon content [13]), indicate that amorphous films are more fragile to the etching process, because of low compacting of the film and weak Si–C bonds generated [9].

To better understand the correlations between carbon content and oxygen addition in SF_6 plasma on etching rates, a mass spectrometry analysis of effluents generated during etching process was performed.

Fig. 6 shows the normalized partial pressure of the SiF_3^+ (correspondent in the mass spectrum to the SiF_4 specie

[13]), CO^+ and CO_2^+ volatile species as a function of O_2% in SF_6+O_2 gas mixture. A good agreement relative to the effect of the O_2% (Fig. 5) can be observed. With the increases of the O_2% a considerable increase of CO^+ and CO_2^+ species is verified, indicating an increase in the etching of the carbon layers. Conversely, it is verified a reduction of the SiF_3^+ peak, indicating that for condition of 80% O_2 the high concentration of fluorine atoms in etching environment is not kept. This effect was constant for all the etched samples.

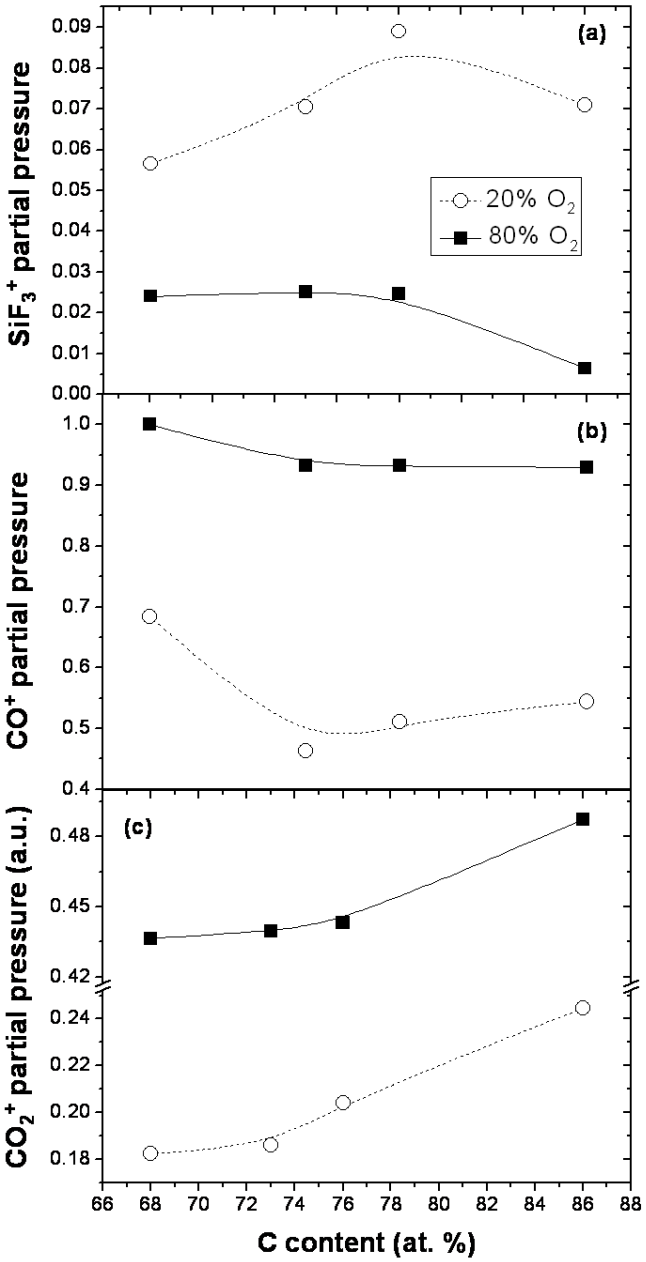

Fig. 6 – The normalized partial pressure of the SiF_3^+ (a) CO^+ (b) and CO_2^+ (c) as a function of O_2 concentration in SF_6+O_2 gas mixture. The intensity was normalized to 1 for maximum value.

Of this fact, we can conclude that for a-Si_xC_y films with high carbon concentration the insertion of a lot amount of O_2 gas in etch environment will go to promote the increase of the etching rate probably for the fact of the Si–C bonds not to be so strong. Thus, the etching of the carbon layers is favored.

Relative to the effect of the reduction of the etching rate with the increase of the carbon content in film, we can observe that SiF_3^+ and CO^+ species follow this trend, indicating a reduction in the extraction of the material of the film during the process.

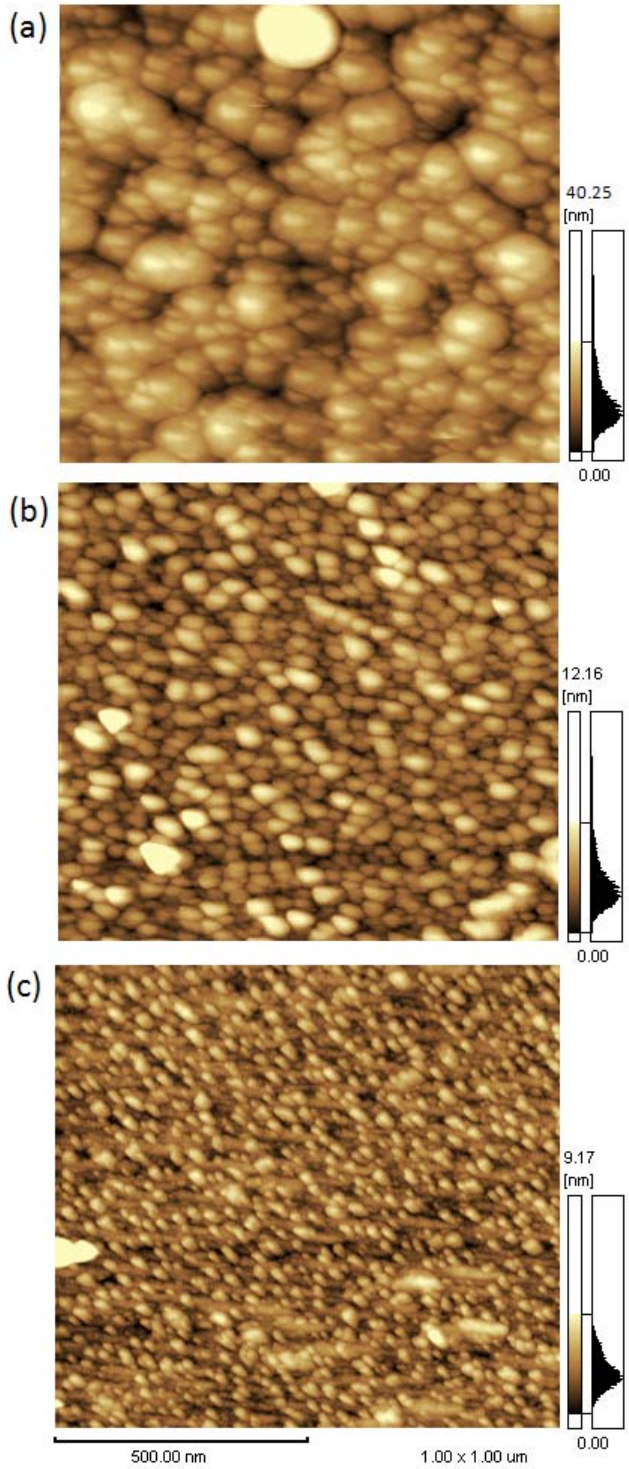

Fig. 7 - AFM dynamic mode image of the surface of a-Si_xC_y film for carbon concentration = 68%: (a) as-deposited, (b) after etching (80% O_2) and (c) after etching (20% O_2). The transverse dimension of the scanned area is 1×1 µm.

3.4 SURFACE MORPHOLOGY

AFM analyses were used to investigate the roughness and morphology of the a-Si_xC_y films as-deposited and after reactive ion etching in SF_6/O_2 plasmas. The RMS roughness of the as-deposited films varied between 5.75 and 6.00 nm. When the film is submitted to the etching process, it was observed a decrease in RMS roughness. This reduction is dependent of the O_2 concentration, for 20% O_2 was observed the lesser RMS roughness values, of the order of 0.75 nm, while for 80% O_2 had been measured values of up to 1.8 nm. Indeed, when the O_2% in a SF_6/O_2 gas discharge is lowered an increase in the polarization potential of the plasma sheath occurs. For the case with 20% O_2 the potential fall in plasma sheath is of the order of 410 V and for 80% O_2 this is reduced for 270V. This fact reflects directly on the energy with that ions reaches the substrate surface and consequently in the final surface roughness. In order to illustrate this effect, Figs. 7(a)-7(c) shows the surface morphology of the a-Si_xC_y film obtained at SiH_4 = 4 sccm for conditions: (a) as-deposited, (b) after etching (80% O_2) and (c) after etching (20% O_2). A surface smoother and free of defects is showed for the case of 20% O_2. Besides, we can notify a wide reduction in the grain size from 70 nm (as-deposited film) to 9 nm (film etched with 20% O_2).

4. CONCLUSION

Non-stoichometric a-Si_xC_y films with high carbon concentration were produced by PECVD technique using SiH_4 and CH_4 as precursor gases. RBS measurements show that the films obtained are actually a compound of silicon and carbon, where the carbon concentration is predominant (> 50%). This result was confirmed by FTIR spectra that indicated the formation of Si-C bonds in the films. Raman analyses confirm the nature amorphous of the films and show that for high carbon content the films exhibit C-C bonds. The etching results showed an increase in the etch rate of the films when the oxygen concentration increases from 20 to 80% in SF_6/O_2 gas mixture. However, for both oxygen concentrations studied, the etch rate decreases with the increase of carbon content in the a-Si_xC_y films. This phenomenology was explained with the use of the mass spectrometry technique. The AFM images show that after etching the surface of the films is smooth and compact.

ACKNOWLEDGEMENTS

The financial support of CNPq is strongly acknowledged. The authors also thank Dr. Marcel Dupret from LAMFI-USP for the RBS measurements, Dr. Walter Miyakawa from IEAv for the AFM analysis, and Dr. Rita C.L.Dutra e Dr. Marta F.K.Takahashi (from IAE-AQI) for FTIR analyses.

REFERENCES

1. ALIZADEH, Z.; SUNDARAM, K.B.; SEAL, S., *Applied surface science* 183 (2001) 270.
2. DI VENTRA, M.; PANTELIDES, S.T., *J. Electronics Materials* 29 (2000) 354.
3. CRACIUN, V.; LAMBERS, E.; BASSIM, N.D.; BANEY, R.H.; SINGH, R.K., *J. of Vacuum Science & Technology A* 19 (2001) 2691.
4. CHABERT, P.; CUNGE, G.; BOOTH, J.-P.; PERRIN, J., *Applied Physics Letters* 79 (2001) 916.
5. LAZAR, M.; VANG, H.; BROSSELARD, P.; RATNAUD, C.; CREMILLIEU, P.; LECLERCQ, J.-L.; DESCAMPS, A.; SCHARNHOLZ, S.; PLANSONA, D.; *Superlattices and Microstructures* 40 (2006) 388.
6. PEREYRA, I.; CARREÑO, M.N.P.; PRADO, R.J.; TABACNIKS, M.H., *Brazilian Journal of Physics*. 27/A (1997) 150.
7. PEREYRA, I.; VILLACORTA, C.A.; CARREÑO, M.N.P.; PRADO, R.J.; FANTINI, M.C.A., *Brazilian Journal of Physics*. 30 (2000) 533.
8. FANTINI, M.C.A.; WUU, D.; HORNG, R.; CHAN, C.; LEE, Y., *Applied Surface Science* 144-145 (1999) 708.
9. OLIVEIRA, A.R.; CARREÑO, M.N.P., *Journal of Non-Crystalline Solids* 352 (2006) 1392.
10. SCHMID, U.; EICKHOFF, M.; RICHTER, CH.; KRÖTZ, G.; SCHIMITT-LANDSIEDEL, D., *Sensor and actuators A* 94 (2001) 87.
11. COSCIA, U.; AMBROSONE, G.; MINARINI, C.; PARISI, V.; SCHUTZMANN, S.; TEBANO, A., *Applied Surface Science*, 252 (2003) 4493.
12. DOLITTLE, I.R., *Nucl. Instrum. Methods Phys. Res*. B 15 (1986) 227.
13. FRAGA, M.A.; PESSOA, R.S.; MASSI, M.; MACIEL, H.S.; SANTOS FILHO, S.G., *ECS Transactions* 9 (2007) 227.
14. HAMMAD, A.; AMANATIDES, E.; MATARAS, D.; RAPAKOULIAS, D., *Thin Solids Films* 452 (2004) 255.
15. CALCAGNO, L.; MUSUMECI, P.; ROCCAFORTE, F.; BONGIORNO, C.; FOTI, G., *Thin Solids Films* 411 (2002) 298.
16. GRACIN, D.; JURAIC, K.; DUBCEK, P.; GAJOVIC, A.; BERNSTORFF, S., *Vacuum* 80 (2005) 98.