Institute of Physics Publishing Journal of Physics: Conference Series **10** (2005) 206–209
doi:10.1088/1742-6596/10/1/051 Second Conference on Microelectronics, Microsystems and Nanotechnology

On the effect of the substrate pretreatment parameters on the composition and structure of plasma deposited SiO_2 thin films

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Abstract. The role of the substrate pretreatment using wet and dry cleaning procedures, on SiO_2 thin film adhesion, integrity and composition was investigated. The SiO_2 depositions were performed in a 27.12 MHz RF plasma reactor and an interelectrode space of 20 mm. The depositions were carried out on different substrates (magnesium, aluminum and c-Si) and at the low temperature of 100 °C. From the wet cleaning methods the use of 5 % HF aqueous solution was found to significantly improve the SiO_2 thin film adhesion in all substrates. Even better results were achieved with the application of H_2 plasma pretreatment, indicating that the etching during the plasma pretreatment results to better conditions for the film growth and the surface step coverage, especially on non-uniform and rough substrates.

1. Introduction

The use of silicon dioxide thin films in many applications as optics, interlayer dielectrics, barrier films for food packaging and corrosion protection layers explains the increasing interest for these films [1-5]. In addition to chemical vapor deposition, several other processes are employed for the deposition of silicon dioxide films. Among these processes, plasma enhanced chemical vapor deposition (PECVD) has become one of the most important thin film deposition processes because of the possibility of preparing good quality coatings at low substrate temperature. One of the most common used organosilicon precursor is tetraethoxy silane (TEOS). The particularity of the deposition through TEOS is that the properties, the structure and the chemical composition of the deposited films are strongly affected by the values of the process parameters and the pretreatment conditions. However, in some specific applications, like in semiconductor device fabrication and in protective layers of metals, a complete removal of C and H from the SiO_2 films is required. A critical factor affecting the deposition of the silicon oxide films is the effect of the pretreatment procedures on the substrates on which the deposition is going to take place.

In this direction, we present the role of the substrate pretreatment using various acidic aqueous solutions as well as the role of substrate pretreatment with H_2 plasma, on SiO_2 thin film adhesion and integrity. The experiments were carried out with the same consumed power and the samples exhibited the best adhesion when cleaned with 5% HF aqueous solution. It was also noticeable that the substrate, which was pretreated with H_2 plasma discharge, exhibited higher resistance to corrosion than those with the aqueous pretreatment and the best step coverage.

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2. Experimental procedure

Film deposition studies have been performed in a capacitively coupled high vacuum (HV) parallel plate reactor with a base vacuum of 10^{-7} mbar. The distance between the two electrodes was 20mm while the temperature of the lower electrode was 373 K. Pressure and flow rate, were independently adjusted by a downstream throttle valve controller and an upstream mass flow and liquid flow controllers, respectively. Liquid TEOS is heated up to 70 ^{o}C and together with O_2/He gas mixture were delivered in the reactor through a showerhead array of holes in the powered electrode. The substrates used, were aluminum alloys (Al 5018), magnesium alloys (AZ91) and c-Si (100).

The real power consumed in the discharge and the discharge impedance was determined by using Fourier transform voltage and current waveform measurements on the RF electrode [6]. Film composition and stability were examined by Fourier Transform Infrared Spectroscopy using a Nicolet 740 FTIR spectrometer with a MCT-B detector and a KBr beam splitter. The quality and the uniformity of the films have been studied by Atomic Force Microscopy (AFM) and Scan Electron Microscopy (SEM) using a commercial Multimode Mode AFM (Nanoscope III, Digital Instruments) and JSM-6300 Scanning Microscope respectively. The corrosion protection properties of deposited film have been assessed by means of electrochemical impedance spectroscopy (EIS). Impedance measurements, carried out by means of a Frequency Response Analyser EIS300 (Gamry Instruments), were performed in 0.1 M NaCl solution as a function of the immersion time.

3. Results and Discussion

The depositions of SiO_x thin films have been performed at total gas pressure of 0.4 mbar, fraction of TEOS in the gas mixture 51 %, intermediate power (39 Watt), frequency of 27.12 MHz and electrode gap of 20 mm. The thickness of the deposited films was in all cases 2 μm. These set of conditions have been reported previously that lead to films with the highest inorganic character and the best adhesive properties [7]. In order to improve further the thin film quality, for the specific set of plasma conditions, different wet and dry pre-treatment processes have been used in order to identify the best way to prepare different substrates for the film growth.

As for the deposition on c-Si substrates, several plasma pre-treatment processes have been applied with different gases (He, He/O_2 and H_2). The best results were achieved with H_2 plasma treatment at relatively high-pressure conditions of 1.3 mbar, rather low nominal power dissipation 30 Watt and treatment times of 30 min. The film deposited on Si (100) substrates after the various pre-treatment processes have been characterized by applying FTIR absorption spectroscopy. Figure 1 shows the infrared spectra in the 500±4000 cm^{-1} range of the as deposited and the H_2 pre-treated films. The spectra exhibit the two characteristic peaks of SiO_2 modes near 800 and 1070 cm^{-1} and absorption bands at 960 and 3450 cm^{-1} assigned to O-H vibration of associated SiOH and water, respectively [8]. In addition, carbon bonding at different forms in the film is identified from Si-C, Si-O-C and C-H stretches located at 880, 1165 and 2970 cm^{-1}, respectively. In order to investigate the effect of pre-treatment on the chemical composition of the thin films and more precisely on the quantity of –OH groups and different A–C (A=Si, O and H) groups, FTIR spectra have been analyzed to the corresponding peaks. Then, the ratios of the area of the A-C peaks versus the area of the Si-O-Si peak and the area of the OH peak versus the area of the Si-O-Si have been calculated and the results are presented in fig.2. It is clearly shown that the pretreatment with hydrogen plasma results to a decrease of the total carbon content present in the deposited films since the ratio, both of Si-C and Si-O-C versus Si-O-Si is significantly lower in this case. The same trend can be observed for the hydroxyl groups present in the deposited film. The removal of the native oxide and moisture from the silicon surface and the possible hydrogen passivation during the H_2 pretreatment seems to be the main reasons for the selective elimination of C and OH groups during the film growth.

In order to further investigate the applicability of the H_2 pre-treatment processes on various substrates, SiOx insulating layers have been deposited on various metal substrates (Mg and Al-alloys). In this case, before the H_2-pre-treatment process different wet cleaning procedures have been applied by altering the acid solvent and concentration (HF, HNO_3, HCl, H_3PO_4) in the cleaning sequence organic - basic - acidic solvent. The best wet cleaning results of metal substrates were achieved when HF of 5 % vw was applied. So, using this wet cleaning procedure, as in the case of c-Si substrates different plasma pre-treatment processes have been applied (He, He/O_2 and H_2). The structure, the quality and the roughness of the metal substrates before and after the pre-treatment were detected by applying AFM and SEM measurements. Hydrogen plasma pre-treatment presented again better results by slightly reducing the surface roughness and by removing contaminants absorbed on the surface, in the time between the wet cleaning and the introduction of the samples to the reactor. The He pre-treatment process had almost no effect on the surface structure while He/O_2 treatment led always to worst results concerning the sample roughness mainly because of the surface oxidation.

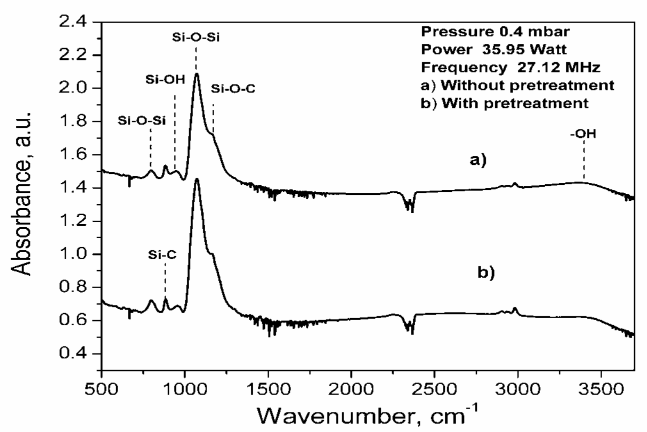

Figure 1. Normalized FTIR spectra for depositions with and without pretreatment

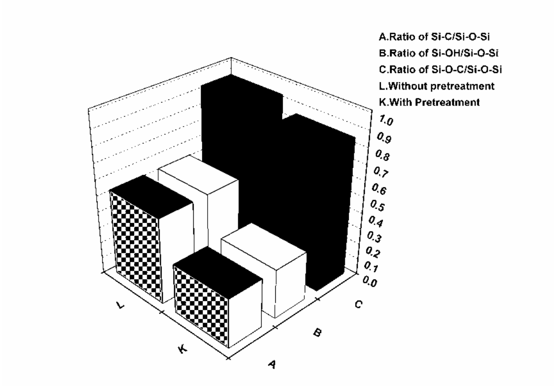

Figure 2. Comparison of the ratios of the Si-C, Si-O-C and the Si-OH peaks versus Si-O-Si peak in the cases of pretreatment and in absence of this process

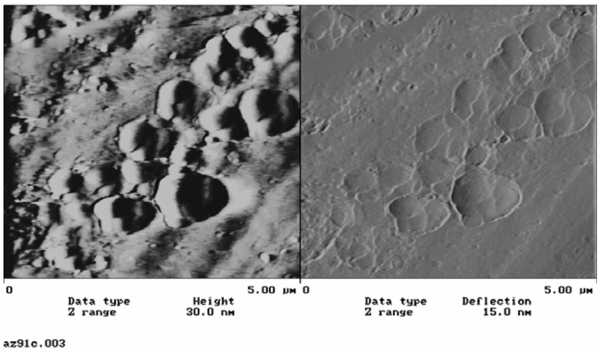

Figure 3. AFM picture of magnesium alloy substrate AZ91 after the deposition of SiO_2 film. The substrate has been pre treated with hydrogen plasma

Furthermore, in conditions of optimal wet cleaning and plasma pre-treated conditions SiO_x thin films have been deposited on various metal substrates. As far as the quality and the uniformity of the film is concerned in figure 3 it is shown an AFM picture of a deposited film on a magnesium (AZ91) substrate while in figures 4 and 5 SEM pictures of a magnesium substrate and a magnesium covered with silicon oxide film are presented respectively. It is rather clear that a good uniformity of the film with nice surface step coverage has been achieved despite the fact of the roughness and the harshness of the substrate. In order to have a quantitative estimation of the thin film adhesion improvement with the application of wet and dry cleaning processes the corrosion resistance of the deposited films was measured by means of Electrochemical Impedance Spectroscopy. Concerning the Mg–alloy (AZ91), the corrosion resistance was found to be improved from 60 Ω/cm^2 for the bare substrate to 2200 Ω/cm^2 for the substrate cleaned only with HF solvent. Application of H_2 plasma treatment further improves the corrosion resistance up to a value of 2700 Ω/cm^2 and consequently the thin film adhesion. The results concerning the Al substrates were much better and the application of wet cleaning and H_2 plasma treatment lead to corrosion resistance values much higher compared to Mg (12500 Ω/cm^2).

These results indicate that the quality and the adhesion of plasma deposited SiO_2 thin films from TEOS/O_2 discharges strongly depend on the kind of the substrate. The choice of a special either wet or dry pre-cleaning process can significantly improve the adhesion of the films in the substrate.

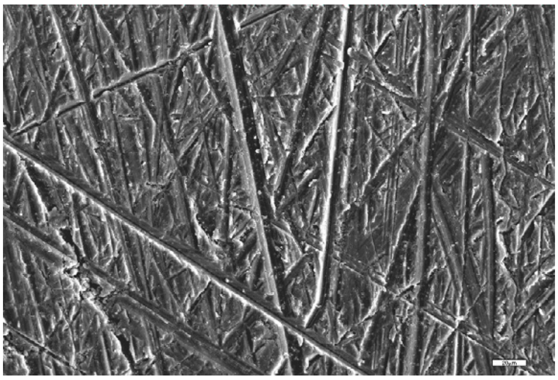

Figure 4. SEM picture of a magnesium alloy substrate (AM 60) before the deposition of the SiO_2 film

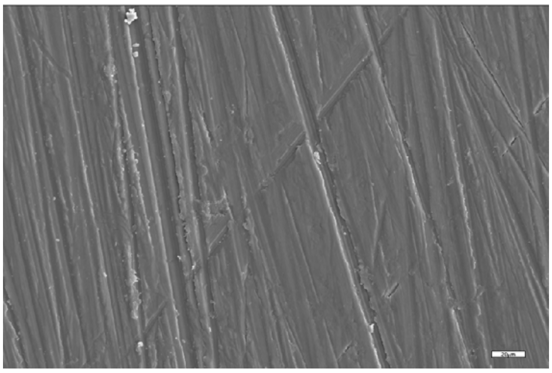

Figure 5. SEM picture of a magnesium alloy (AM 60) substrate after the deposition of the SiO_2 film (pre treated with hydrogen plasma)

4. Conclusions

An investigation of the substrate wet and dry pretreatments effect on the chemical composition and the structure of the SiO_2 thin films deposited from TEOS/O_2 discharges on various substrates (c-Si, Mg- and Al-alloys) was carried out.

Among the dry cleaning processes, the use of hydrogen plasma pretreatment was found to significantly lower the total carbon content and the hydroxyl groups presented in the film from the composition films of the film point of view. In addition, H_2 pre-treatment improves the adhesion of the films on extremely rough surfaces. Concerning the wet cleaning processes, the treatment with 5 % HF presented the best results but worst compared to the plasma treatment processes.

The effectiveness of both plasma and wet cleaning processes was found to strongly depend on the kind of the substrate, but H_2 plasma pre-treatment of samples was found in all cases to be a good solution for improving the adhesion of SiO_2 deposited thin films.

5. References

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