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Etching Rate Analysis of a SiO_2 Wafer with Argon Ions in XPS

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Abstract

In this report we describe the process of obtaining a depth profile of a thin SiO_2 film – growth through the RTA process – done by ARXPS and XPS. Also, the method of sputtering the sample, with Ar gas, in order to clean the sample from organic contaminants, obtain the etching rate, and imperative properties of the transection is reviewed.

Keyworks: Depth Profile, XPS, ARXPS

1. Introduction

There is a considerable amount of processes, techniques, and equipment for working on surface and thin layer analytics of materials; for instance: the auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and Rutherford Backscattering Spectroscopy (RBS) [1]. Nevertheless, the maximum depth that these processes can analyze are about 10 nanometers [2]; hence, it is necessary to sputter part of the sample if inner layers are needed to be studied. The benefits on working on depth profiles and etching processes are varied as they can reveal the amount of a dopant or a contaminant is present in the sample; it could also be used to clean the surface of the sample from organic contaminants, such as carbon or oxygen [3].

In order to have a successful depth profile analysis done by XPS, numerous factors must be considered, such as the vacuum in the chamber during the etching process; as the better the vacuum, the better are the results. The energy of the incident ion beam and its components also play an important role – generally, Xe is the best gas that could be used for the etching process, however, many opt for the second-best gas, Ar, as the latter is cheaper [3,4]. Finally, an angle-resolved X-ray photoelectron spectroscopy (ARXPS) is imperative in order to be able to determine varying thickness of different layers and therefore its etching rate; this technique,

consists in varying the angle of the sample inside the XPS in order to detect different ranges of energetic electrons so a calculation of thickness and composition of the film can be performed [5].

It is important to have into consideration the fact that the longer the etching time and the higher the energy of the beam, the deeper the crater that will be created; the risk of not paying enough attention to it could lead to a loss of key information of the material being studied [4].

On the other hand, combining a sequence of ion gun etch cycles with XPS analyses provides quantified information as well as layer thicknesses. Before removing material from the sample, a spectrum, or set of spectra, is recorded from the surface of the sample. The surface is etched by rastering an ion beam over a square or rectangular area of the sample. After the etch cycle, the ion beam is blanked, and another set of spectra is recorded. This sequence of etching and spectrum acquisition is repeated until profiling has proceeded to the required depth. During the profile acquisition, the acceptance area of the source-defined monochromator beam should be directed at the center of the area rastered by the ion beam, which ensures that the analyzed areas are situated on the flat bottom of the crater [3].

In this report, we describe the results of a depth profile analysis done to a Si wafer after being subjected to a rapid thermal annealing process for more than 30 minutes at an approximate constant temperature of 900 ºC (more details about the process can be found in our last report *Rapid Thermal Annealing Process Applied to a Silicon Wafer and Characterized by ARXPS Method* [6]).

2. Experimental

2.1 Materials

For the rapid thermal annealing process, the sample was taken to the University Center of Exact Sciences and Engineering (CUCEI) of University of Guadalajara. The method required a tube, which was about 1.2 m large, made of quartz connected to a muffle; and a ventilator that injected air at a pressure of 1 atm. For the characterization, depth profile analysis, and etching processes; we used ITESO's X-ray photoelectron spectroscope.

2.2 Methodology for the XPS Manipulation

In order to obtain the depth profile of the SiO2 film, a process suggestive in class were followed which can be synthetized in five steps:

1. Creation of a survey, at a 0° angle, to register the present elements at the surface of the film – notice that organic contamination is expected.

2. Etch the sample, considering a desirable area for the upcoming ARXPS analysis, until the organic contamination is no longer observed. The proposed time of etching is about 20 s.

3. Etch periodically until silicon is present with orbital 2p (0). The proposed engraving time for this step is approximately 5 minutes.

4. Etch the sample until oxidized layers of silicon (Si 2p (+4)) are not observed, an ARXPS analysis is performed after each engraving interval. The proposed time of etching for this step is about 5 to 10 min interval.

5. Stop the experimental procedure when bounds of oxygen with silicon are no longer detected and proceed with the data analysis.

The angles for the ARXPS method will be of 0°, 5°, 15°, 25°, 35°, 45°, and 55°. The proposed steps, in fact, depict the general logic for a modest monoatomic depth profiling of a common film in material science, which can be appreciated in figure 1.

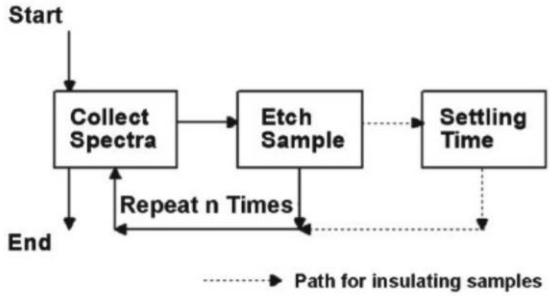

Figure 1. General steps for a monoatomic depth profiling process; specialized for insulating samples. Image retrieved from *Thermo Scientific* [3].

Due to the time required to successfully generate a depth profile of the Si sample, the task was

disseminated within our 25-member class; thus, six different teams were created to work on a different step. Our team was particularly responsible for the fourth step.

2.3 Methodology for the Data Analysis

In order to obtain the desired information for the depth profile and etching rate, it is imperative to gather each one of the files of the ARXPSs and use them to determine the thickness of the sample at that moment. Once the thicknesses are determined, their difference values are divided by the time interval of etching used in that instance. Namely,

$$ER = \frac{\Delta \text{thickness}}{\Delta \text{time}}$$

Where ER stands for etching rate.

3. Results and Discussion

The conditions in which the experimental method was developed were varying within the steps. On the second step, the voltage and current used to etch the surface of the sample were of 1000 V and 36 µA, respectively; for a 1x1 mm^2 area. Whereas for the other steps, the voltage and current used were of 3000 V and 36 µA, respectively; for a 5x5 mm^2 area. The vacuum used for each analysis were values near to $3.0x10^{-9}$ mbar.

3.1 XPS-Manipulation Results

As expected, there was a considerable amount of organic contamination in the surface of the sample, as there was a substantial detection of carbon, such that its auger was also noticed. Figure 2 shows the survey.

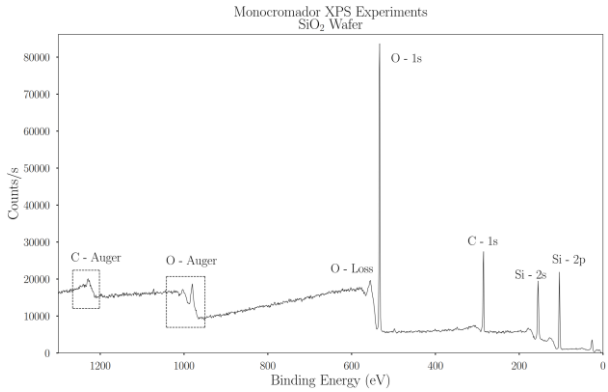

Figure 2. Resultant survey of the first step.

3.1.1 Fourth Step

Once the 2p silicon peak was observed, a first etching of two and a half minutes was made, and a survey was carried out to see the change in the right peak of the 2p silicon. As stipulated in the methodology, the ARXPS analysis was performed after the etching. Due to the low peak growth it was decided to carry out the next etching with a duration of 5 minutes as can be seen in Figure 4 (S2). Despite the rise in time, the peak did not increase considerably, so a new 5-minute etching was made but without performing the ARXPS analysis between these two surveys.

Table 1 shows the surveys that were performed, the pickling times and when the ARXPS analysis of the sample was performed. The selection of the total pickling times was made among the teammates attending the experiment considering the growth of the right silicon 2p peak.

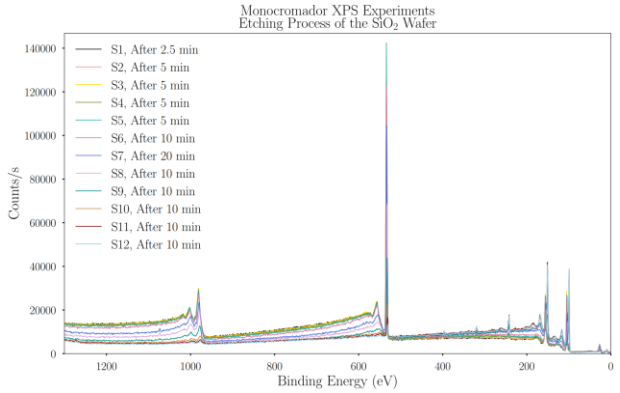

Figure 3. Surveys done during our contribution of the project and each of their etching time that created them. S stands for survey.

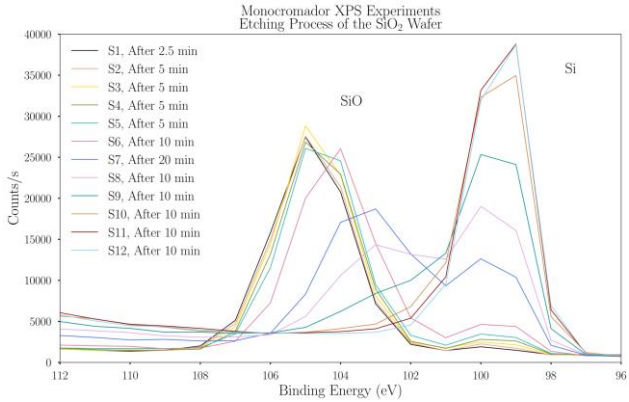

Figure 4. Close ups of the surveys for the peaks of interests: silicon with oxygen and pure silicon.

	SURVEY	ETCHING TIME	TOTAL ETCHING TIME
ARXPS1 →	Survey 1	After 2.5 minutes	2.5 minutos
	Survey 2	After 5 minutes	10 minutos
	Survey 3	After 5 minutes	
ARXPS 2 →	Survey 4	After 5 minutes	20 minutos
	Survey 5	After 5 minutes	
	Survey 6	After 10 minutes	
ARXPS 3 →	Survey 7	After 20 minutes	20 minutos
ARXPS 4 →	Survey 8	After 10 minutes	10 minutos
ARXPS 5 →	Survey 9	After 10 minutes	10 minutos
ARXPS 6 →	Survey 10	After 10 minutes	10 minutos
ARXPS 7 →	Survey 11	After 10 minutes	10 minutos
ARXPS 8 →	Survey 12	After 10 minutes	10 minutos

Table 1. Step 4 measurement chart.

3.2 Data Analysis

To investigate the properties of the sample, we made use of the programs Excel and AAnalizer; as well as the programming language Python.

3.2.1 Fourth Step

By considering the ARXPS results, we were able to retrieve information about the thickness of the sample at the time after it was bombarded with Ar during a given period of time; as shown in figure 4.

For the etching number 10, respective to our survey number 1, the angular results are shown in figure 5.

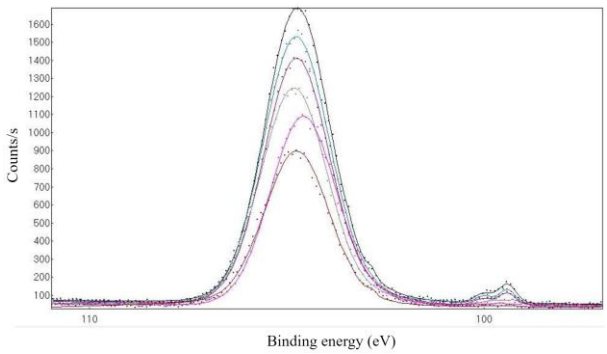

Figure 5. High resolution of silicon respecting to our survey 1.

After working on the analysis, the results yield a thickness of about 15 nm respecting to a 150 s of constant bombarding, after it was etched for 2475 s. Furthermore, the survey number three yield a thickness of 12.44 nm after being bombarded during 300 s with a total etching time of 3075 s. In addition, survey number 13 depicts a thickness of approximately 9.24 nm, after being bombarded during 1200 s with a total etching time of 4275 s. Figure 6 display the angular results of the latter event; which it can be appreciated how the expected behavior is proceeding: the bounded silicon peak is decreasing whereas the pure silicon peak is increasing.

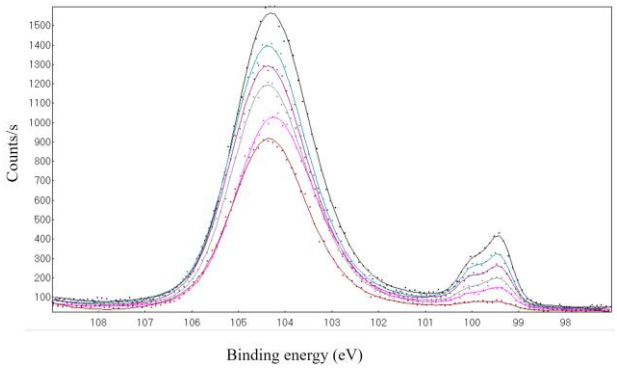

Figure 6. High resolution of silicon respecting to our survey 13.

3.2.2 General Results

With the incorporation of all the data obtained by the rest of the teams, it was possible to calculate imperative parameters of the sample; such as the etching rate, the depth profile of silicon pure and attached to oxygen, as well as pure oxygen, and carbon. These properties are shown in figure 7.

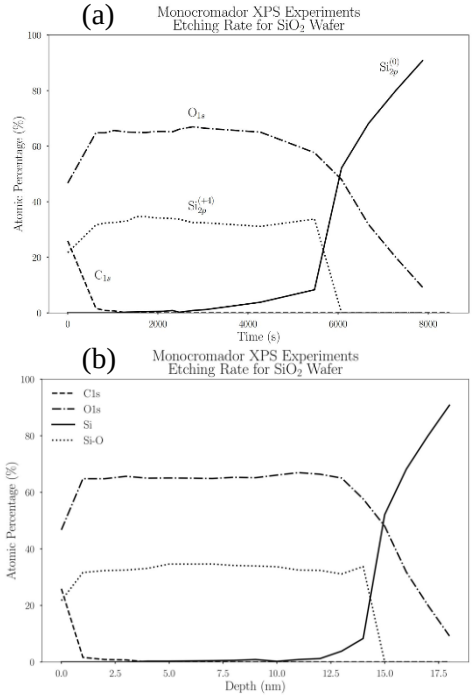

Figure 7. (a) General results for the etching rate and (b) the implications of etching in the depth of the sample per percentage of present-element.

In order to synthetize the behavior of the peaks regarding to silicon, a graph of its intensity vs binging energy within their change in etching time was created, shown in figure 8.

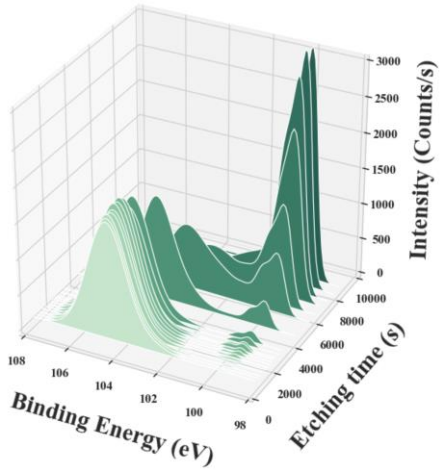

Figure 8. Intensity of the high-resolution silicon peaks and its alteration during the etching process. The peak that increases (dark green) corresponds to the pure silicon, whilst the one that decreases (light green), correspond to the silicon attached to oxygen.

4. Conclusion

After having it consulted, it turned out that the method in which we were determining the time to etch the sample was not so appropriate, as more analysis could be driven in order to determine if more time was needed to properly etch the sample. In other words, figure 4 shows no adequate criterion to resolve how extensive is the crater becoming. Instead, it is suggested to drive an ARXPS analysis to compel the effectiveness of the etching.

Besides, it is worth mentioning that we succeed in observing the expected behavior in the development of the experimental method; the set of data could have been improved after assigning more ARXPS analysis, however, it would have meant spending more resources in the laboratory – specially time and money.

On the other hand, we would like to stress the gravity of not previously defining the precedent by which the data were to be stored: as it led to a loss of relevant time and efficiency of work. Hence, we encourage, for similar forthcoming laboratory practices, to hitherto dispose an arrangement on how to designate names the resultant files.

5. References

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