Modified RCA Silicon (Si) Cleaning

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Abstract

Silicon wafers were cleaned with a chemical washing process (RCA), which consists in series of interleaved rinses of distinct pH solutions and deionized water.

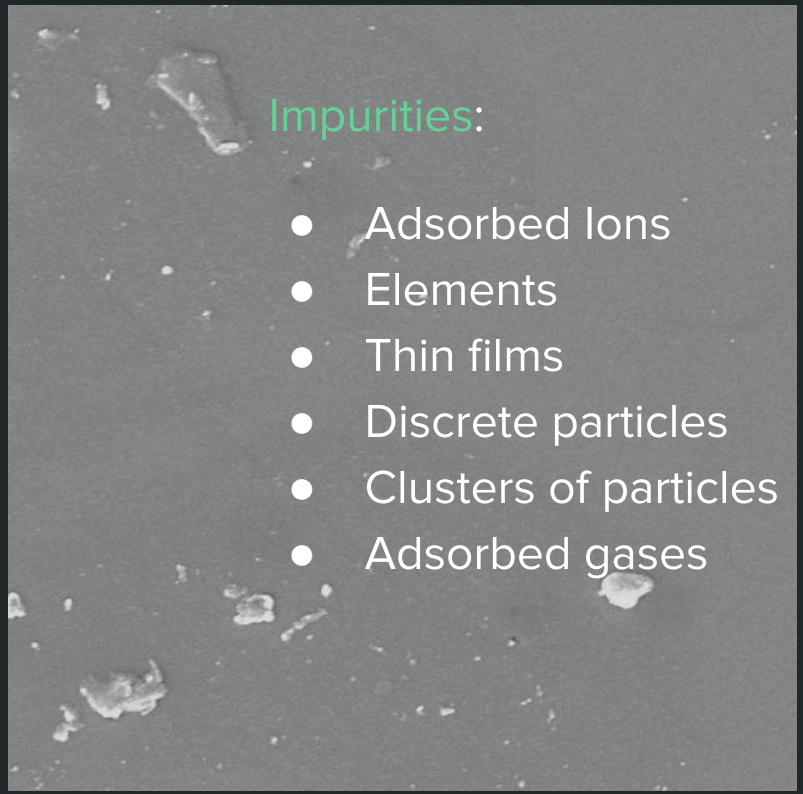
Characterized by:

- XPS: to obtain information about the elemental composition and chemical bondings.

Introduction

The importance of having clean substrate surface of semiconductors has been recognized since the year 1950.

- Reliability
- Product Yield
- Increased device performance



Introduction

Objective: Removal of particles and chemical impurities from the surface without damaging the substrate.

PROBLEMS:

- Expensive
- Wafer breakage
- More debris is deposited

Early techniques:

- Organic solvent extraction
- Boiling nitric acid
- Aqua Regia
- Concentrated hydrofluoric acid
- Hot acid mixtures
- Plasma
- Ultrasonic in detergent
- Vapor phase
- Supercritical fluid
- Brush scrubbing
- ...

Introduction

In 1965 at the Radio Corporation of America (RCA) Werner Kern developed a cleaning chemistry process.

It is a process accepted worldwide as the standard clean for silicon wafers.

RCA process:

Efficient at removing contaminants such as organics and metals.

Based on a two-step oxidizing and complexing treatment with hydrogen peroxide solutions.

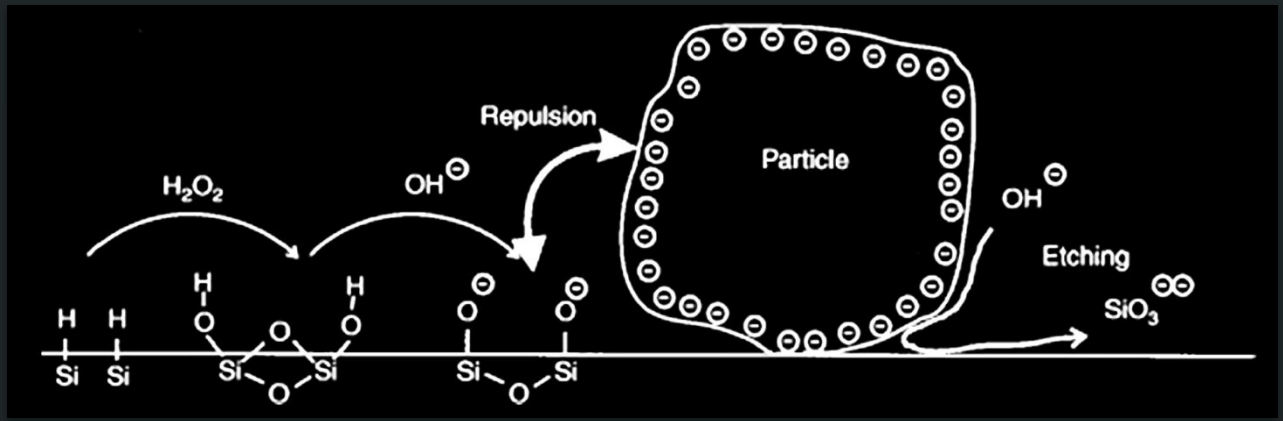
Reaction Chemistry Oxidation potentials Reagent purity Reagent volatility Safety Economy

Introduction

RCA

RCA Process: SC-1

- First Step (SC-1): Alkaline mixture at high pH for removal of organic contamination.



Introduction

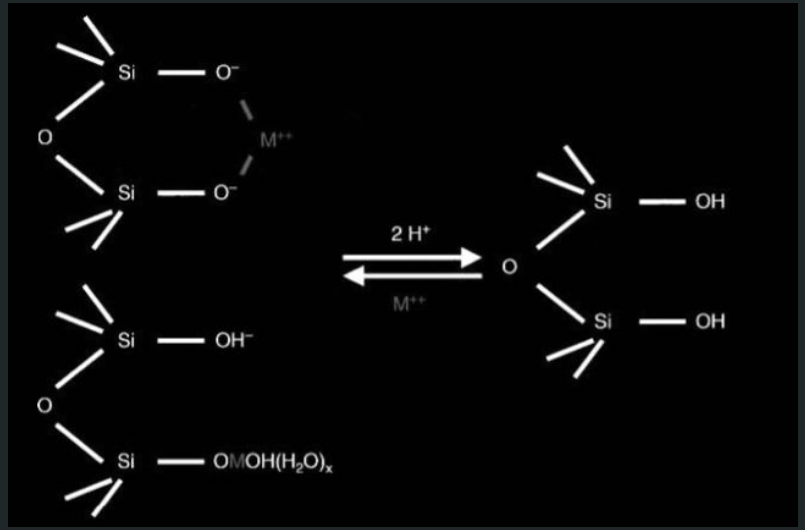
RCA Process: SC-2

- Second Step (SC-2): Acidic mixture at low pH for removal of metal and ionic contaminants

Au, Cr, Cu, Fe, Ag, Ni, Cd, Zn, Co and Al^{3+}, Fe^{3+}, Mg^{2+}

Introduction

RCA Process: SC-2



Metal ions are usually bonded on the SiO2 layer via SiOM bonds or as insoluble salts.

They can be exchanged with protons to form sianol groups freeing M^2 due to an equilibrium reaction (pH must be low).

H_2O_2 is present to oxidise metal in metallic form so it can be dissolved.

Introduction

Modified RCA Process:

There are several RCA-based cleans derived from the original:

- H_2SO_4 and H_2O_2 can be used as a preliminary clean up treatment
- Another step concerns an etch in HF solution for bare silicon wafers (prior to SC-1)

*Intermediate rinsing steps with deionised (DI) water are used for cleaning to assure low ionic contamination like:

$[NH_4]^+$, Na^+, K^+, Cu^+, Fe^{3+}, Zn^{2+}, Cr^{3+}, Mn^{2+} or Br^-, Cl^-, $[NO_2]^{2-}$, $[NO_3]^-$, $[PO_4]^{3-}$, $[SO_4]^{2-}$

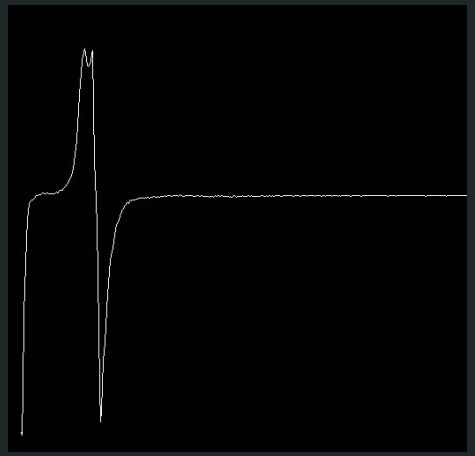
Introduction

Measurement of contamination

Auger spectroscopy can determine changes on characteristic energies related to change of chemical composition of the surface.

Adsorption of gases
Contamination of Surface
Chemical bonds with atoms on surface.

It is simpler and faster than XPS



Experimental Procedure

Washing

Sulfuric Acid (H_2SO_4)

Fluorhydric Acid (HF)

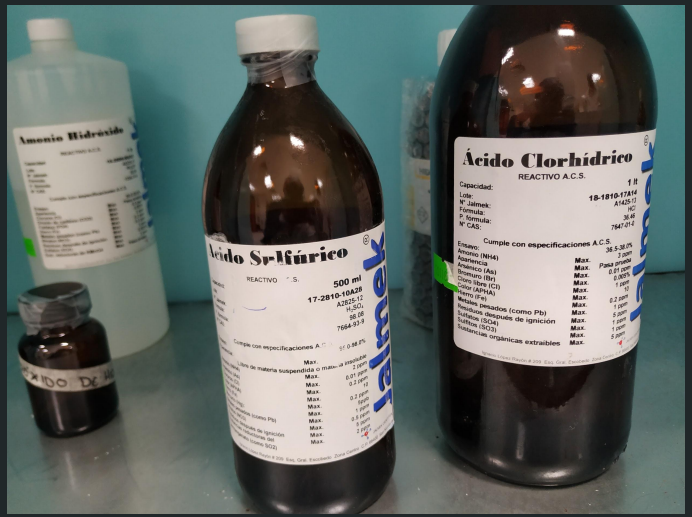
Deionized Water (Di)H_2O

Oxygen Water (H_2O_2)

Ammonium Hydroxide (NH_4OH)

Chlorhydric Acid (HCl)

Reactives



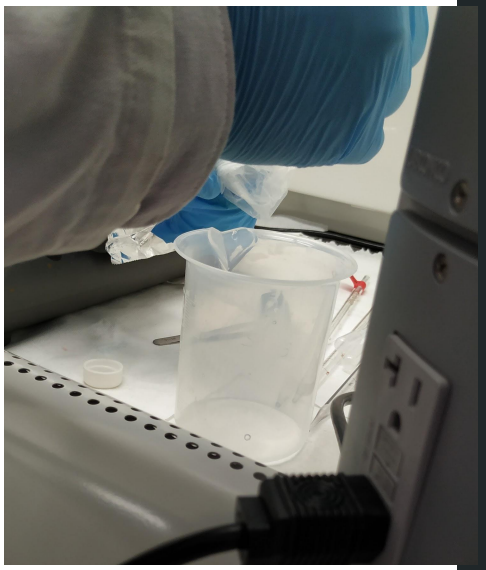
Washing

1.- In a beaker, pour 30 mL of H_2SO_4, heat at 65°C and add 5 mL of H_2O_2. Let the solution heat to 85°C during 10 minutes. Stir it at all times.

2.- “Running” deionized water rinse of Si at room temperature during 1 minute.

Washing

3.- In a plastic bucket, pour 20 mL of H_2O, 5 mL of HF and 5 mL of H_2O_2 at room temperature for one minute.

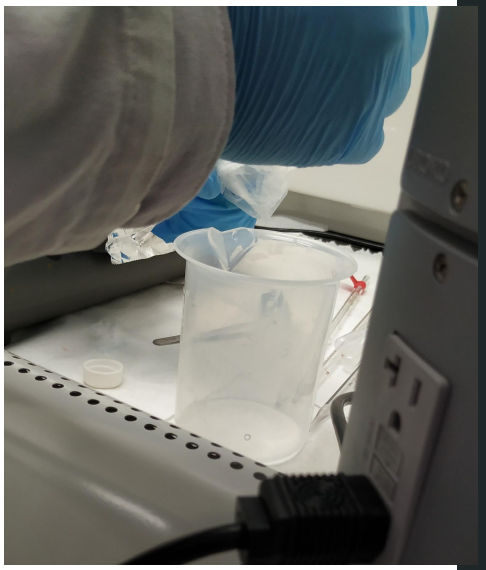


4.- “Running” deionized water rinse of Si at room temperature during 1 minute.

5.- In a beaker, pour 25 mL of H_2O, 5 mL of NH_4OH and heat at 60°C. Then, add 5 mL of H_2O_2 and heat at 80°C during 5 minutes more. Stir solution at all times.

Washing

6.- “Running” deionized water rinse of Si at room temperature during 1 minute.



7.- In a beaker, pour 30 mL of H_2O, add 5 mL of HCl and heat until 60°C. Then, add 5 mL of H_2O_2 and heat at 85°C during 10 minutes. Stir solution at all times.

8.- “Running” deionized water rinse of Si at room temperature during 1 minute.

Characterization

XPS

Conditions:

- Pressure of the Analysis chamber: 1.69E-9 mbar
- Al K-Alpha Source (1487.6 eV)

The surface composition of Si, C and O structures was analized with XPS (SPECS).

Results and discussion

XPS Analysis

ALso, on the XPS analysis we obtained the sample's pocertunal composition. It can be notice that the % Atomic from the oxygen and the silicon oxide does not match.

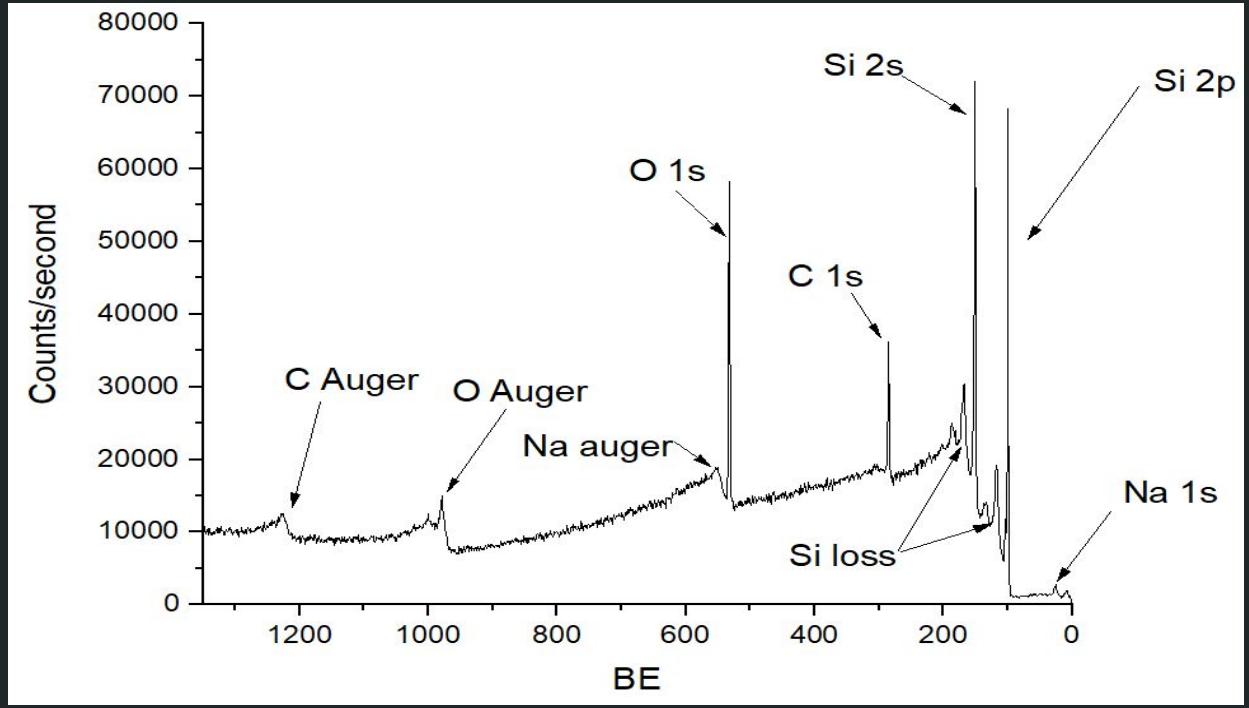
Core level	Kinetic Energy (KE)	Binding Energy (BE)	Scofield Factor	Peak area (lij)	Ni	% Atomic	%Atomic/Element
C 1s	1202.03	284.68	1	2550.72	17.81	22.90	25.19
C 1s	1200.27	286.44	1	255.67	1.79	2.30	
O 1s	954.26	532.45	2.93	7632.92	21.38	27.49	27.49
Si 2p	1387.52	99.19	0.817	7458.77	3.30	4.25	47.32
Si 2p	1387.04	99.67	0.817	868.55	14.88	19.13	
$Si(O_2)$ 2p	1383.86	102.85	0.817	628.48	18.62	23.94	
					77.79	100.00	100

$$Ni = \frac{AREA(lij)}{(Scofield)x(KE)^{0.7}}$$

$$\%Atom = \frac{(Ni)x(100)}{\sum Ni}$$

Results and discussion

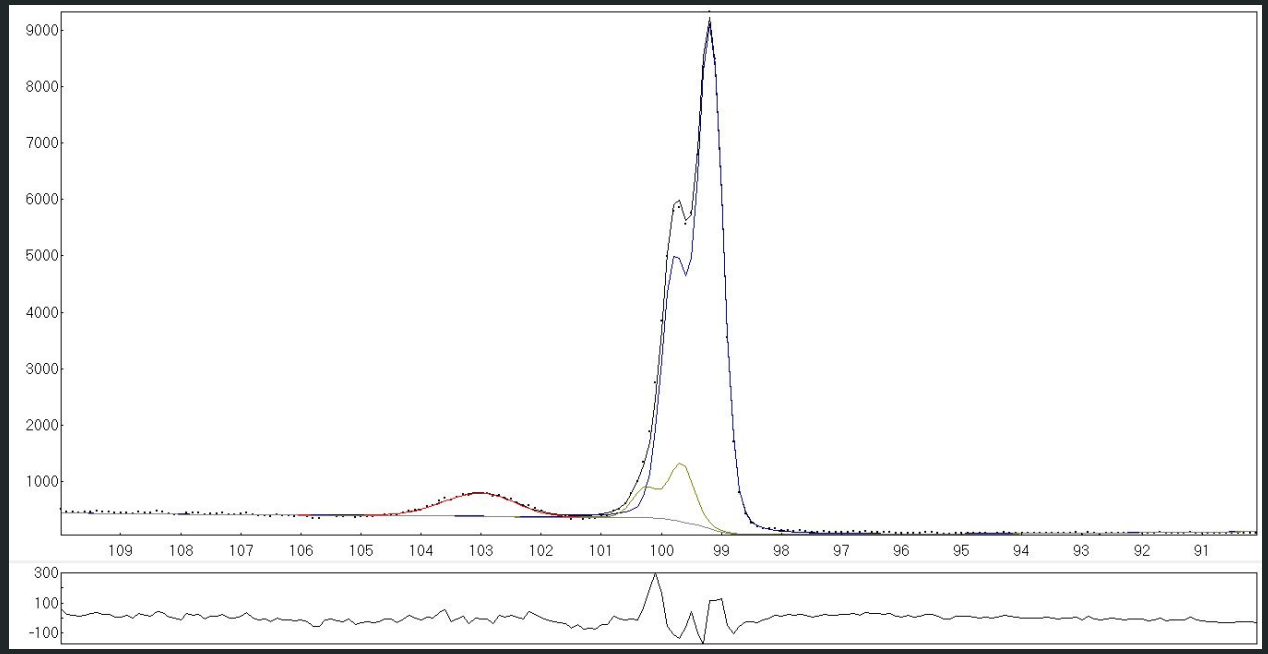
XPS Analysis



In the general spectrum survey we can find which elements have presence on our XPS sample.

Results and discussion

XPS Analysis

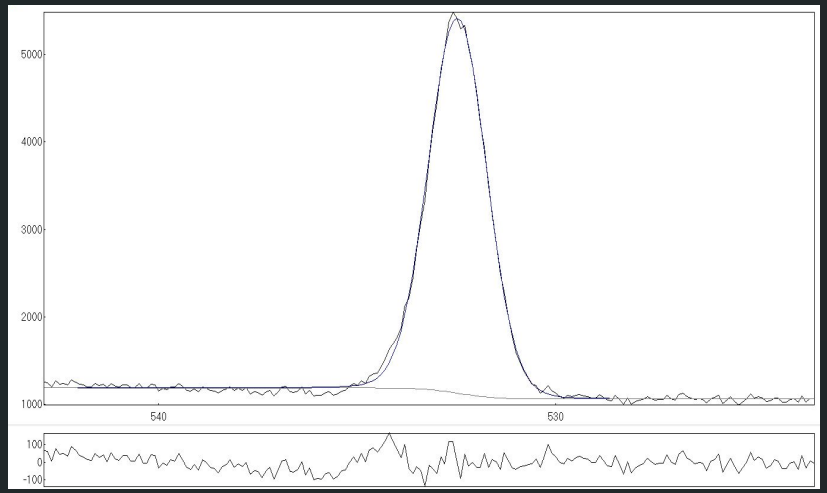


XPS spectra. Si 2p high definition peak

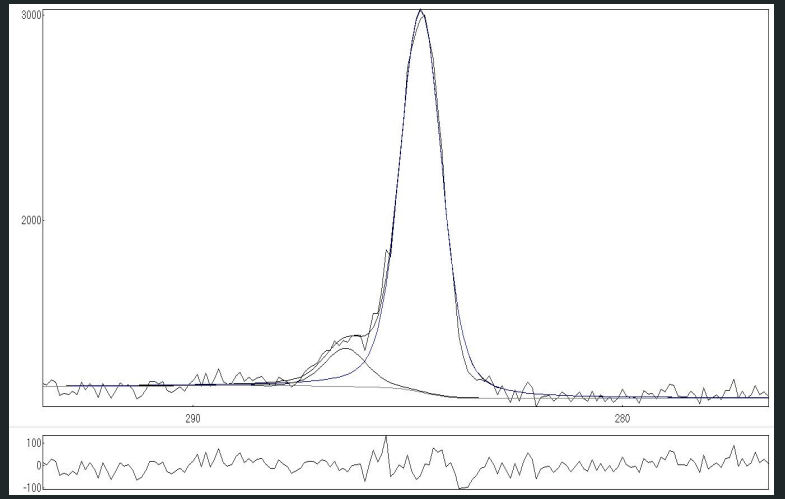
With this high definition peak, we can assume that we had silicon oxide, due the red peak.

Results and discussion

XPS Analysis



XPS spectra. O 1s high definition peak

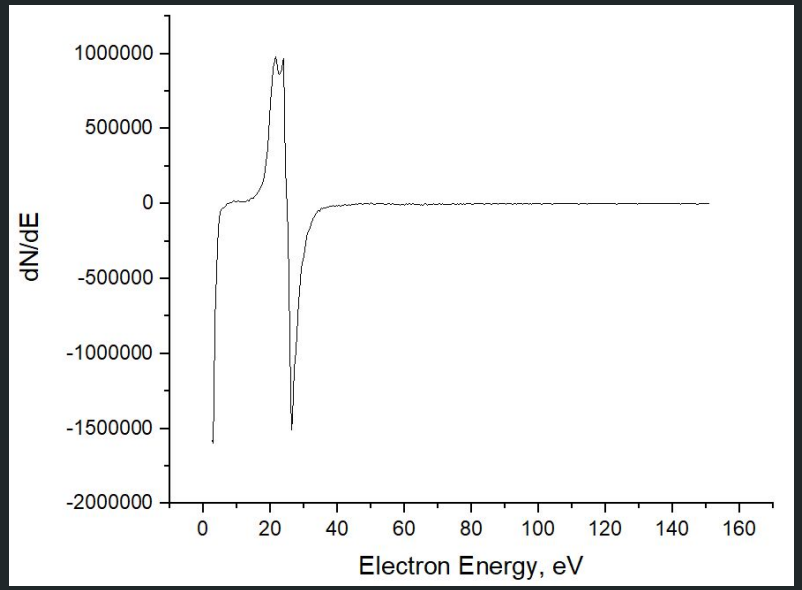


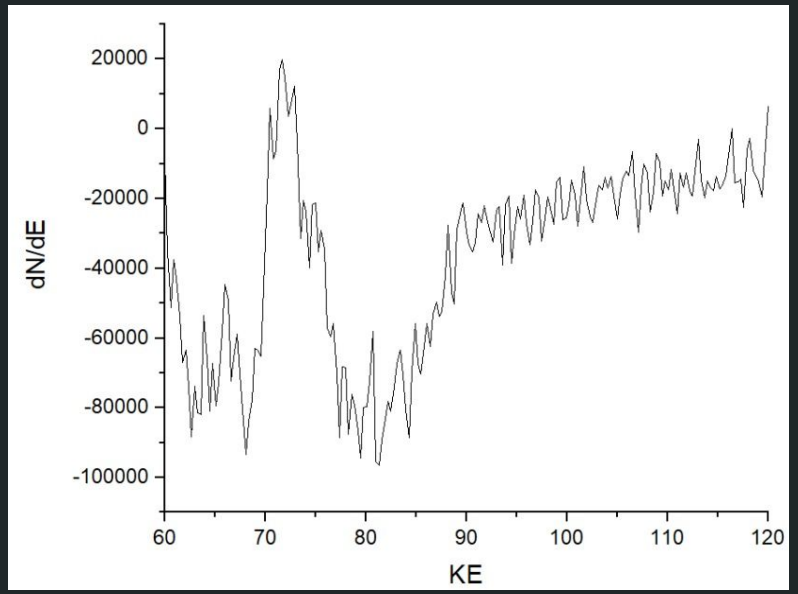
XPS spectra. C 1s high definition peak

By the high definition analysis we can say that we had not enough oxygen for the Sio_2.

Results and discussion

Auger Analysis

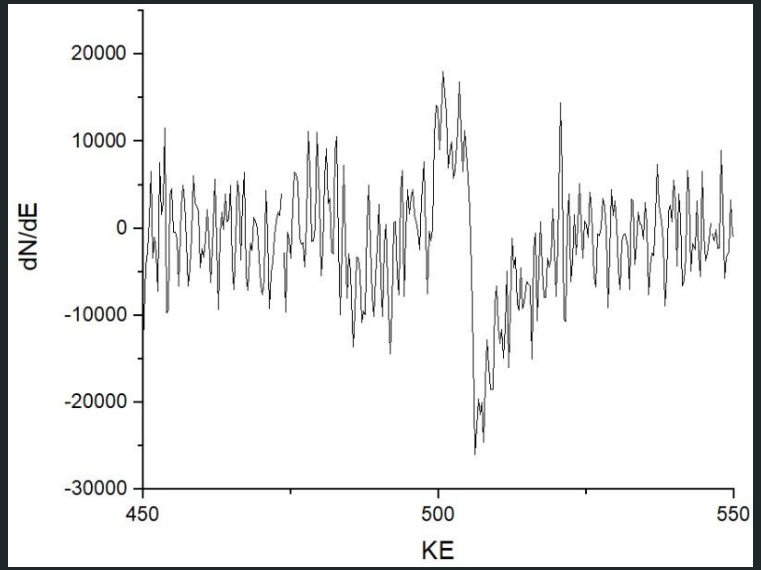


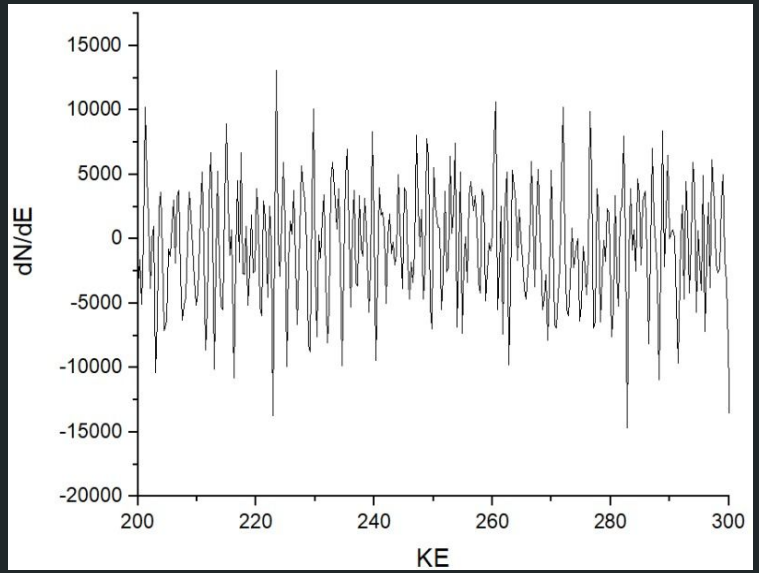


Auger Si peak, before (left) and after (right) oxidation. We can observe that it does not correspond to the references, so it can be assume that the Auger measurement system its uncalibrated.

Results and discussion

Auger Analysis





Auger O and C peaks, oxygen (left) and carbon (right). Also we can observe that it does not corresponds to the references.

Conclusions

It is imperative to manipulate with care the samples cleaned with RCA method because it is time consuming and it involves certain risks.

Analysis of the surface concluded that the sample was contaminated. This might have been because measurements were done a week later.

Layer of Silicon oxide was formed over time.

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