Mechanism of Processes Stimulated by Ultraviolet Radiation

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Abstract. Modern technologies for creating integrated circuit elements offer many innovations, both in terms of the technological cycle and the introduction of new technologies. Stimulated processes in this regard and their mechanism require a thorough study in order to further improve the technology and the parameters of the micro and nano devices made on their basis. We have studied the processes stimulated by ultraviolet radiation, such as Stimulated Plasma Anodizing and Stimulated Magnetron Sputtering. In the study of stimulated mechanism should be considered processes which are going on with ultraviolet irradiation on the sample and plasma. In these processes, the UV light effects on the plasma, on the surface of the synthesized material, its volume, and the interface area of the material. In particular, in the case of plasma anodizing, UV radiation: 1) produces ozone in the plasma that is much more active than oxygen ion. 2) Ionizes interface area of Plasma-oxide, producing additional current carriers, and 3) transferring electrons from the oxidized material bond zone to the anti-bond zone, thereby weakening the bond strength between the oxide atoms. Because of these effects, the process of mixing anions and cations is facilitated and, consequently, the oxygen diffusion coefficient is increased and the oxidation process is accelerated. At the oxide-semiconductor interface happens roasting existing charge trapping levels, which reduces the concentration of charge carriers and improves the oxide parameters. The same processes are observed in the case of Magnetron Sputtering. In the deposited layer excites mechanical tensions and it can be removed by UV irradiation in the same way as in the case of plasma anodizing.

1. Introduction
The process of plasma anodizing takes place applying a positive potential to the sample, with respect to the plasma, thereby migrating the negative ions (anions) of oxygen released from the plasma into the growing oxide. The mutual migration of anions and cations in the substrate increases the thickness of the oxide from the plasma side. According to Faraday’s law each ion has its own contribution to the formation of the oxide, which is characterized by the number of transfer $\nu^-$ for anions and $\nu^+$ for cations. In general $0<\nu^-<1$, also $0<\nu^+<1$ and righteous $\nu^- + \nu^+ = 1$. As the oxide film increases, the $\nu^+$ decreases, and consequently the efficiency of oxide formation decreases. To increase efficiency, the process needs to be stimulated by high temperatures, or some other technic. One of these technics was to use the ultraviolet light in the plasma anodizing process, which increases the efficiency of the process several times and improves the oxide parameters [1]. In order to develop a stimulated plasma anodizing mechanism, the processes that take place during ultraviolet (UV) light irradiation in the process of plasma anodizing should be considered. In these processes, UV light effects on the...
migration of anions and cations in the plasma, in the surface of the substrate, in the volume of the substrate and in the material-semiconductor interface.

2. Experimental data and Theoretical discussion

To study the mechanism of stimulated processes were performed Plasma anodizing to receive hafnium and titanium oxides. Processes were performed with and without UV light to highlight the role of UV radiation on stimulated processes. The oxide growth kinetics are shown in Figure 1.

The growth kinetic showed the rate of growth for HfO₂ to be 12nm/min with UV light and 3nm/min without UV light. Also in the case of TiO₂ - 13nm/min with UV light and 3nm/min without UV light.

It is well known [2], that UV radiation in the plasma generates ozone, which is carried out by the reaction:

\[ 3O_2 \text{ UV, } \lambda=180\text{nm} \rightarrow 2O_3 \]  

(1)

In the ozone molecule, both O — O bonds have the same length of 1,278Å and angle between them is 116.8°. The central atom of oxygen is sp²-hybridized. Ozone and oxygen are very different in chemical properties. Ozone composed by oxygen atoms is endothermic, it has excess energy, it easily emits one oxygen atom and reveals much more active oxidizing property than the oxygen molecule [3]. Ozone oxidizes almost all metals (except platinum and iridium).

On the interface of plasma-oxide UV irradiation ionizes oxygen molecule by the reaction:

\[ e + O_2 \rightarrow O^- + O \]  

(2)

resulting in obtaining additional charge carriers [4], which further accelerates the process of oxide formation. UV irradiation in the process of forming an oxide film causes moving the electrons from the oxidized material’s bonding (π3d) zone into the anti-bonding (σ4s) zone (Figure 2), thereby weakening the strength of the bonding between the oxide atoms.
Figure 2. Energy diagram of molecular orbitals consisting of titanium and oxygen atoms

As a result of this process, accelerates the process of mixing anions ($\nu^-$) and cations ($\nu^+$) and increases the oxygen diffusion coefficient [5]. Theoretically, in real crystals, it is possible to diffuse oxygen by vacancy or by interstitial (it belongs to Huntel) methods (Figure 3).

Figure 3. a) Oxide structure in lattice, b) mechanism of Huntelian diffusion.

The vacancy mechanism of diffusion oxygen atoms requires a lot of energy, however, for the formation of transition metal oxides, it is necessary to have two vacancies with the main atom, which is less probably. Therefore, this process is going very slowly.

One type of interstitial diffusion, so-called the mechanism of Huntelian diffusion, requires less energy, therefore it is more likely than other mechanisms of diffusion [6], (Figure 3). When the "Huntel configuration" is created, the main atom and oxygen are placed around the knot, dividing one "quantum knot" each to other and exist between two neighboring knots.

Such an arrangement of atoms is energetically advantageous, and their existence in space is real. A polar ionic bond is formed, because the main atom and oxygen have different electronegativity. Then
the Huntel disintegrates and a new Huntel is created: one of the Huntel fits into the knot and the other - moves to the neighboring knot and forms a new Huntel, oxygen-knot complex and vacancy. As a result, will be created a new orientated Huntel. Then it is possible to: a) disassemble the huntel again and create a new one, etc. Huntel's movement in the crystal takes place; b) to the neighboring of the main atom comes an oxygen atom and makes a bonding with a single valence electron to Huntel's basic atom and forms an "oxide". Relatively it is difficult to break such a bond and overall is obtained more stable and equilibrium state of the oxide structure.

It is important that the shifting of the Huntel configuration in the distance of the lattice period is accompanied by the movement of all the atoms in the Huntel at a smaller distance than the lattice period. This circumstance makes it easier to realize the diffusion of interstitial atoms by Huntel mechanism.

All processes mentioned above, are considered as independent processes and the probabilities of creating diffusion jumps can be multiplied. Creation of the Huntel configuration is characterized by 

\[ e^{\frac{E_G}{kT}} \] 

factor, where the \( E_G \) is an activation energy of generated Huntel. By the applying external \( U \) voltage and with Huntel’s coordinate number \( n \), the frequency of Huntel's jump will be:

\[ f = \frac{2\pi n \mu U}{S} e^{\frac{E_G}{kT}} \]  

(3)

where \( \mu \) is a mobility of the complex.

It can be seen that the diffusion rate of the complex and the oxygen depends not only on the temperature, but also on the activation energy of the complex in the lattice, mobility and the magnitude of binding energies to neighboring atoms, which are determined by external factors. In our case, the action of UV-light reduces the \( E_G \) potential energy and increases \( \mu \) mobility of the complex. According to formula (3), the temperature helps the process of plasma anodizing. When other technological parameters are constant, the frequency of formation and disintegration of the Huntel complex is low on the small values of external voltage (low current densities of oxide formation) and the thickness and velocity of oxide formation are low. In the case of high voltage, the complex moves so that the probability of its decomposition is small and thereby is not obtained a stable oxide complex. It should be noted that similarly to our results and explanations, authors [7] observed a sharp increase of the oxygen diffusion rate during silicon oxidation with UV irradiation when the temperature did not exceed 300°C. To explain this phenomenon, the authors [8] believe that the "bridge" created in Si-O-Si is energetically advantageous to create a triple oxygen configuration. If an anion of oxygen is placed in this configuration, then the bonding between the two oxygen atoms breaks (by attraction and by irradiation) and creates a new bridge. By creating and dissolving such a bond, oxygen ions migrate to SiO\(_2\). It has been calculated that at such jumps, the effective potential wall is 0.27 eV and 0.11 E for O\(^-\) and O\(^{2-}\) ions respectively. The motion of such a configuration explains the increase of oxygen diffusion coefficient. In oxide-semiconductor interface is going roasting of the existing charge trapping levels, which reduces the concentration of charge carriers and improves the oxide parameters.

The mechanism of affect ultraviolet light irradiation on the substance has been successfully transferred on live organisms, particularly on viruses. The fundamental elements in the reproductive system of all microorganisms are nucleic acids - deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). These genetic materials contain chemical bonds and compounds. The DNA molecule is made up of two interconnected threads connected by four pins: adenine (A), cytosine (C), guanine (G), and thymine (T) (Figure 4). Nucleic acids that make up DNA and RNA absorb ultraviolet radiation at
wave length interval of 220 ÷ 290 nm. Ultraviolet radiation induces thymine dimerization in the DNA molecule, violating the sequence and disabling the whole mechanism.

Figure 4. Structure of DNA before UV irradiation and after UV irradiation.

They survive for some time after ultraviolet radiation, but no longer have the ability to damage, renew or undergo mutations other live organisms. Therefore, ultraviolet radiation kills viruses and destroys their ability to multiply. It should be noted that this mechanism applies to the cells of any live infectious organisms.

3. Conclusions
A possible physical mechanism for ultraviolet light-stimulated processes has been developed to explain the increase oxygen diffusion coefficient in the oxide at low temperatures; the action of the UV light on the plasma, on the surface of the synthesized material, its volume, and the interface area of the material. Also, the effect of UV irradiation on live microorganisms was shown. UV destroys chemical bonds between nucleic acids and damages their ability to multiply.

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