

ULTRAVIOLET LASER-INDUCED OXIDATION OF ANTIMONY: CHEMICAL COMPOSITION AND GROWTH KINETICS OF THE OXIDE LAYER

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The effects of UV (193 nm) laser irradiation of antimony in the atmosphere on the kinetics of oxidation and on the oxide stoichiometry have been studied using a quartz microbalance and X-ray photoelectron spectroscopy. An absolute calibration of the quartz microbalance enables us to measure quantitatively the kinetics of the oxygen uptake on a thin film; while XPS results indicate the evolution of the superficial chemical composition of the oxide layer grown on single crystals. At sufficiently low fluence to prevent any thermal effect ($\leq 3 \text{ mJ/cm}^2$) we observe a sharp increase of the oxidation rate and the laser grown oxide layer contains more Sb_2O_3 than the native or the thermal oxides. We show that the oxidation is enhanced at low fluence mainly by a mechanism involving electronic excitations into the oxide layer, or of the adsorbed molecules, but not by an optical excitation of the molecules in the gaseous phase.

1. Introduction

The oxidation of metals has been the subject of a considerable number of studies [1]. The photochemically activated processes in Laser Enhanced Oxidation (LEO) of metals and semiconductors [2,3] require a better basic understanding. The mechanisms of the thermal oxidation are yet largely documented in the literature and LEO can be considered like a model reaction paving the ground for the understanding of diffusion mechanisms stimulated by light, involved in laser chemical vapour deposition, in laser induced reactive etching for cold and local laser material processing [4], and in experiments of local diffusion induced by lasers.

The peculiar interest of this study stems from the fact that it could contribute to elucidating the recent observation of LEO of GaSb(111) surfaces under the same conditions. As a matter of fact, the GaSb single crystals were covered by their native oxides which are known to be a solid solution of gallium and antimony oxides [5,6]. On the other hand, antimony is a semimetal with rhombohedral lattice symmetry and several oxidation states [7,8].

The oxide layer formed in the presence of oxygen may consist of various oxides, the relative concentration of which may be indicative for the growth mechanism.

In air, Sb_2O_5 decomposes at 600 K to Sb_2O_3 [9]. The oxidation of Sb and Sb compounds starts very fast but is limited [10,11].

2. Experimental conditions

The samples were irradiated in the atmosphere, at room temperature, at repetition rates lower than 3 Hz with multiple exposures.

The 2000 Å thick polycrystalline [12] Sb film was evaporated (rates: 5–15 Å/s) on a quartz crystal kept at room temperature in a vacuum better than 10^{-9} Torr. The thin film remained 15 min in air before suffering the first irradiation. We paid particular attention to measuring the resonance frequency after the quartz had reached thermal equilibrium.

For XPS studies we used freshly cleaved (111) surfaces of high purity Sb single crystals. The HP 5950 A electron spectrometer possesses a mono-

chromatized AlK α ($h\nu = 1486.6$ eV) X-ray source. In fig. 1 we show the Sb4d $_{5/2}$ signals appearing at the lowest binding energy (metallic state). A computerized fitting program resolves and measures quantitatively the intensities of the Sb4d line coming respectively from metallic, III and V valence atoms (fig. 2). The final accuracy was estimated to

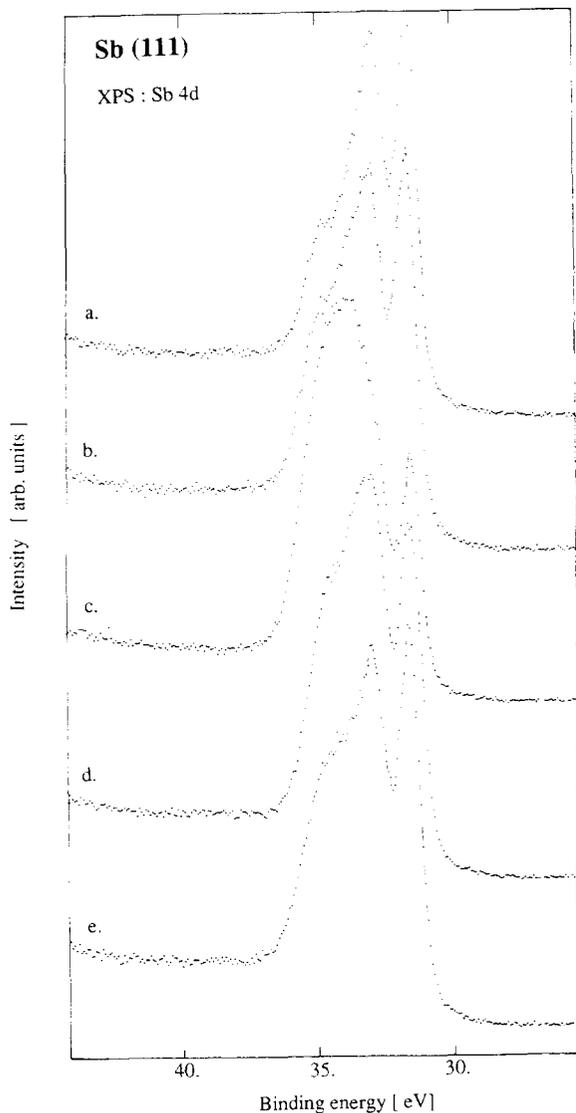


Fig. 1. Sb4d XPS lines from five Sb(111) surfaces. (a) Freshly cleaved in air; (b) oxidized one hour in air at room temperature; (c) oxidized one month under the same conditions; (d) oxidized 50 min in air at 90°C; (e) oxidized 20 min at room temperature in an atmosphere enriched with ozone.

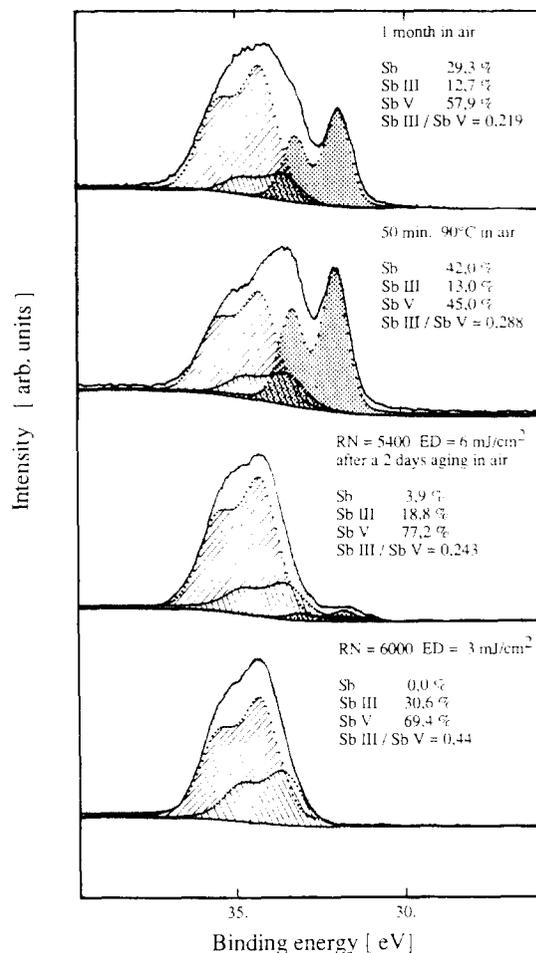


Fig. 2. Fittings of Sb4d XPS lines for four differently oxidized Sb(111) surfaces; showing successively, while increasing the binding energy, the electronic signal intensities from Sb atoms in the metallic state and in Sb₂O₃ and Sb₂O₅ oxides.

be better than 5%. The lack of a proper fitting technique led other authors to an incomplete characterization and to ambiguities in the interpretation of the oxide composition [6,10,14].

3. Experimental results

3.1. Oxidation of Sb in air at room temperature and at 90°C

In UHV, after evaporation, the weight measured on the microbalance remains very stable

over hours. Whereas nitrogen does not adsorb on Sb [13], the adsorption of oxygen is dissociative and leads to oxidation. The microbalance shows that the first oxidation step goes very fast as soon as the air enters the vacuum vessel. During the first 90 s in the atmosphere the weight increases at a constant rate of about $0.4 \mu\text{g}/\text{cm}^2 \cdot \text{min}$. This value drops rapidly down to $0.0076 \mu\text{g}/\text{cm}^2 \cdot \text{min}$ after 10 min, and the kinetic law becomes linear. The total weight increase after the first half hour is $1.1 \mu\text{g}/\text{cm}^2$, and the kinetic data show a change of slope that could be explained by the completion of an oxide layer by a process of seeding and progressive coverage of the surface, or to the combination of kinetic characteristics of the various crystallographic planes constituting the surface. The kinetic law remains linear with a slope of $0.0014 \mu\text{g}/\text{cm}^2 \cdot \text{min}$ for at least the next 10 hours. At that moment the increase of the weight reaches $1.9 \mu\text{g}/\text{cm}^2$.

The microbalance can also measure the amount of gas which is adsorbed or desorbed from the surface when the film is brought into the air or when it enters the vacuum. This amount is characteristic of both the specific area and the sticking coefficient of oxygen. We measured an increase of the superficial weight of $1.0 \mu\text{g}/\text{cm}^2$ when the metallic film is exposed to air. The same increase was observed when a well degassed oxidized film enters again the air. Since the metallic surface is expected to be more reactive, this observation could be explained by a structural modification taking place during the nucleation of the oxide layer, and by an increase of the film roughness. Moreover an oxidized surface maintained in vacuum for 30 min loosed $1.5 \mu\text{g}/\text{cm}^2$. Since the Sb oxides do not sublime at room temperature, we observe probably a slow desorption of the oxygen molecules which are either trapped in superficial microporosities or in the grain boundaries, or dissolved into the oxide layer.

The XPS spectrum in fig. 1a was obtained for an Sb single crystal cleaved in air and placed into vacuum within 10 min. The decrease of the intensity of the metallic signal after respectively one hour (fig. 1b) and one month (fig. 1c) in air at room temperature confirms a fast start of the oxidation followed by a slow down. Fig. 1a is

properly fitted assuming a composition of 57.6% of metallic atoms, 16.3% of atoms with valence III, and 26.1% with valence V. Comparison with fig. 2a shows that during the first step the oxidation produces more Sb_2O_3 , and that the Sb_2O_5 concentration increases thereafter. The oxide with the lowest content in oxygen is expected to be in contact with the semimetal, whereas the highest content is near the surface. As a matter of fact, Sb_2O_5 is more stable than $\text{Sb}_2\text{O}_3 + \text{O}_2$ ($\Delta H = 33.1 \text{ kcal/mol}$). The relative decrease of the Sb_2O_3 signal intensity during the oxide growth is consistent with the model of the growth of a multilayered oxide.

Comparison of the intensities of the photoelectron signals from the bulk (I_{bulk}) and from the top oxide layer (I_{oxide}) provides an approximation of the thickness (a) of the oxide layer, assuming a continuous oxide layer with a sharp oxide-semimetal interface:

$$\frac{I_{\text{bulk}}}{I_{\text{oxide}}} = \frac{\exp(-a/\lambda)}{1 - \exp(-a/\lambda)}, \quad (1)$$

where the mean free path (λ) of the photoelectrons from the measured core levels is about 25 \AA . The oxide layer on the freshly cleaved sample is found to be 13 \AA thick, and to grow to 23 \AA after one month.

A moderate temperature rise promotes the oxidation rate. Surface analysis of a sample kept 50 min at 90°C in air (figs. 1d and 2b) shows that electrons from the substrate still escape the surface through the oxide layer and the composition is still consistent with a multilayered oxide.

We observed no significant effect on the rate of oxidation after having irradiated a thin film of Sb for 10 hours in air by the continuous red radiation of a 0.5 mW He-Ne laser.

3.2. Oxidation of Sb in the air under UV light irradiation

Fig. 3 shows that the oxygen uptake into the oxide layer is proportional to the number of irradiations. The whole exposure to the UV light lasted 220 min with a constant repetition rate of 1 Hz and a fluence of $2.5 \text{ mJ}/\text{cm}^2$ for each irradiation. The weight density increase is 2.5 times more

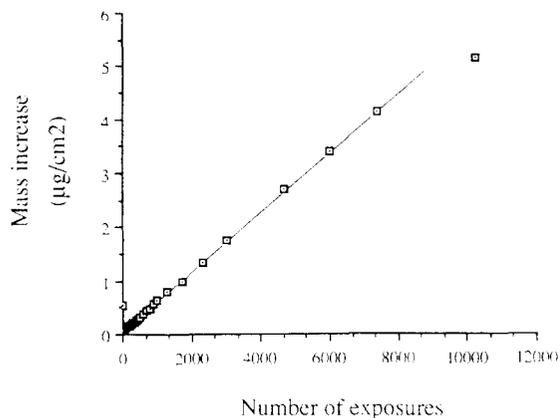


Fig. 3. The linear increase of the weight density of an Sb thin film evaporated onto a quartz microbalance, during its oxidation in air under pulsed UV irradiation. The fluence on the film was 2.5 mJ/cm^2 per exposure to the laser beam, with a repetition rate of 1 Hz.

important than after more than 10 hours of conventional oxidation. The slope of the linear kinetic law did not change up to an increase in weight of the order of 5 µg/cm^2 . The rate was 21 times higher than under free oxidation conditions (0.0294 µg/cm^2 per min), which corresponds to a quantum yield of 37×10^{-4} adsorbed oxygen molecule per incident photon, or to an uptake of 1.5% of a monolayer of adsorbed O_2 per irradiation.

During the first few minutes (first tens of irradiations), two fast mechanisms compete: (i) the conventional early course of oxidation which saturates rapidly, (ii) the photochemical enhancement which lasts over thousands of irradiations.

The attenuation of the signal from the substrate (fig. 4) shows that one thousand irradiations (10–15 min) oxidize the surface of the crystal more than after one month of free oxidation in air (fig. 1c). This result is apparently not in quantitative agreement with the kinetic data measured with the quartz microbalance. The discrepancy is caused by a faster free oxidation of the polycrystalline film, probably due to porosities or fractures appearing in the oxide layer, or to oxygen diffusion along the boundaries of the metallic or oxidized grains. The increase of the rate of oxidation under UV light irradiation is, however, so high that this effect does not influence too much the absolute value measured under these condi-

tions. Finally, since the ratio $I_{\text{bulk}}/I_{\text{oxide}}$ on spectrum 4e, is lower than 0.01, the oxide layer must be at least 115 Å thick, and it must cover the surface completely.

The oxide layer grown under laser irradiation contains an anomalous relative concentration of Sb_2O_3 with respect to the layer grown under near-equilibrium conditions (fig. 2d). Fig. 2c shows that

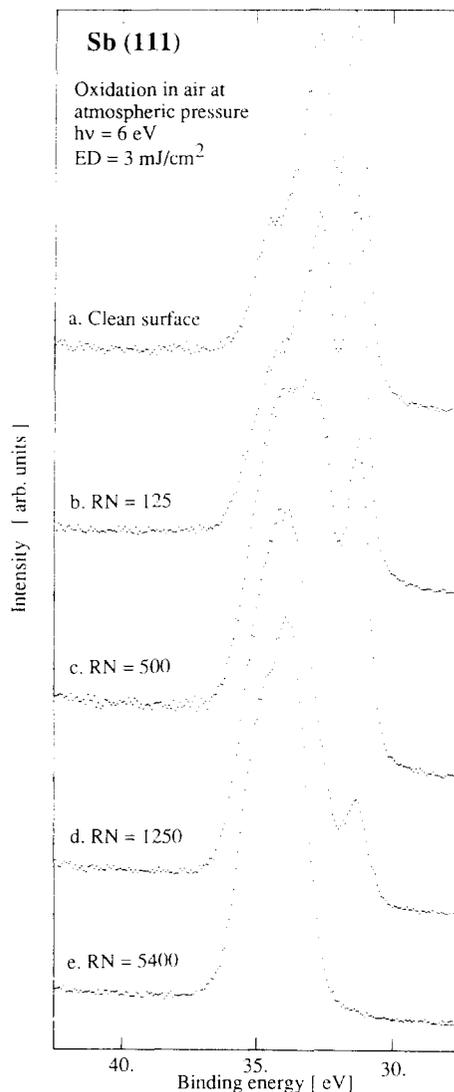


Fig. 4. Sb4d lines of five Sb(111) surfaces oxidized in air at room temperature under low fluence UV light irradiation. The RN parameter denotes the number of exposures to the laser beam.

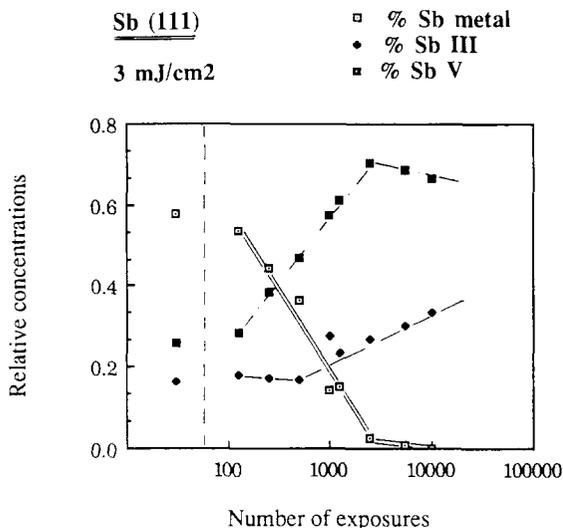


Fig. 5. Variation of the relative signal intensities of the V, III, 0 valence contributions to the Sb4d line versus the number of irradiations. The fitting procedure used for the signal processing is described in the text. For reference the analysis performed on a freshly cleaved sample is given on the left hand side of the picture. Laser fluence 3 mJ/cm². (□) Percentage Sb metal, (◆) percentage Sb III, (■) percentage Sb V.

the oxide films grown under UV light irradiation seem to reach the “equilibrium” stoichiometry described previously when aged in air.

The exponential increase of the intensity of the photoelectronic signal of Sb₂O₅ conjugated to the exponential decrease of the one related to the substrate (fig. 5) is highly consistent with a layer by layer growth of an Sb₂O₅ layer on the top of the Sb₂O₃ layer during the first 500 irradiations, and corresponds to the initial growth stage. Assuming a sharp oxide–substrate interface, we calculate at that time a total thickness of 25 Å for the oxide layer. The increase of the Sb₂O₃ relative concentration after further irradiations provides evidence of a change of mechanism for the oxidation reaction, which coincides with a less accurate fitting of the XPS data for surfaces irradiated between 500 and 1300 times. A good fitting can be obtained by considering the existence of a non-stoichiometric oxide with an intermediate valence (IV) in relative concentrations lower than 5%. These observations and the latter decrease of the Sb₂O₅ relative concentration shows that the Sb₂O₃ layer grows at the expense of the Sb₂O₅ layer.

Under atmospheric conditions other constituents of the atmosphere (CO₂, ozone, N₂O, ...) may produce some specific oxidizing species. However we believe that the direct excitation of gaseous molecules not adsorbed on the surface does not contribute significantly to the activation of the reaction. As a matter of fact, first we present on fig. 1e the XPS analysis of a surface exposed to an atmosphere enriched in ozone by the laser beam itself, paying attention that no UV light can reach the sample. The sample is placed in the spectrometer only half an hour after the preparation. Second, since the areas shadowed by the ledge of cleavage steps less than 100 μm in height are not fully oxidized even after 10000 irradiations, the UV light must have a very localized effect. Third, we measured that 17.4% of the intensity of the UV beam at 193 nm is absorbed on a path 1 m long in the atmosphere. 35×10^{-6} incident photons are absorbed on a path 200 μm from the surface. This proportion is two orders of magnitude lower than the quantum yield measured for the uptake of the oxygen molecules. A larger reaction volume would be in contradiction with the high localization of the LEO effect and should imply a thickness of gas much larger than the mean free path of the molecules in the atmosphere. Finally, most of the photons are absorbed into the oxide layer which has a band gap of 4.2 eV [15].

4. Discussion

4.1. Free oxidation of Sb

The experimental observations can be explained in a very comprehensive way if the rate determining mechanism is assumed to be the adsorption–dissociation step.

The fast early step of oxidation is favoured by the dissociative adsorption of the oxygen molecules on the semimetallic antimony surface. The dissolution of atomic oxygen in the Sb crystal does not require a local dilatation of the crystalline lattice of Sb [7,16], and leads to the formation of chained Sb₂O₃ molecules laid on the surface according to the structure of the Sb₂O₃ crystal

[17]. The Sb_2O_5 molecules are formed by saturating superficial Sb atoms with doubly bound oxygen atoms. The adsorption of oxidizing molecules on the Sb native oxides is not dissociative any more. The sticking coefficient for the oxygen molecules is reduced because of a lack of metallic sites for chemisorption.

After this first course, the kinetic law becomes linear and shows no saturation for long term oxidation, suggesting the formation of a discontinuous or volatile non-protective oxide film. As a matter of fact, the Sb native oxides start evaporating in vacuum at 500 K [16]; so, even at moderate temperature, the oxide molecules may have high mobility on the antimony surface. Moreover the oxide molecules may be found in a triangular bipyramidal structure or may have sp symmetry. The former is the most stable, although the activation energy to flip to the other is quite low (~ 100 kJ/mol) by the so-called "Berry" and "turnstile rotation" mechanisms [8]. Finally, the large difference between the lattice parameters of the substrate and the oxide may cause important strain during the oxide layer growth. The increase of the specific area of the thin film might indicate that disordering and cracking takes place, or that porosity develops. The faster oxidation of the thin film is probably due to a larger specific area of the polycrystalline samples and to diffusion of the oxygen molecules along the grain boundaries.

4.2. Oxidation of Sb under UV light irradiation

The usual fast first step of oxidation is observed. The UV light obviously opens a new path for the oxidation reaction with a fast linear kinetics (not limited by diffusion [1,13]). When the oxide layer grows, the oxide becomes poorer in oxygen and the observation of non-stoichiometric oxide (Sb_2O_4) might give evidence for the decomposition of Sb_2O_5 molecules. Finally the Sb_2O_3 layer in contact with the substrate grows at the expense of the Sb_2O_5 layer. During the aging in air we observe the saturation of the superficial Sb sites reduced during the growth of the Sb_2O_3 layer.

At low fluences the effects of the laser beam cannot be explained by a thermal process. As a matter of fact, we calculate a maximum superficial

temperature rise of the Sb single crystal of 30°C under irradiations with a fluence of $3\text{ mJ}/\text{cm}^2$, and a temperature rise of 108°C for the polycrystalline samples deposited onto quartz under the same fluence. Moreover, enhancement of the oxidation rate due to heating of the crystalline sample in air at similar temperatures does not lead to a similar increase of oxidation. There are other evidences that the LEO of antimony is obviously associated to optical electronic transitions into the oxide: (i) most of the light is absorbed in the oxide layer, (ii) the stimulation is highly localized, (iii) illumination with red photons shows no effect on the rate of oxidation.

The following mechanisms have been proposed to explain the opening of a new reaction path by the UV light [3]:

(i) The light could directly dissociate some molecules adsorbed on the surface, and it might reduce the activation energy barrier for the break-up of the Sb bond into the substrate. The second mechanism, driven by diffusion of vacancies, should be characterized by a parabolic kinetic law [1,13], and will not be considered. The direct interaction of light with any molecules present in the atmosphere has been ruled out as a significant process in section 3.2.

(ii) The UV light could increase the sticking coefficient of oxygen and produce new oxidizing species at the surface (O^{2-}, \dots) by injecting electrons into the conduction band of the oxide. However, a preferential growth of the Sb_2O_5 oxide would be expected from such a mechanism.

(iii) Itoh's model [18] predicts that an electronic excitation could induce a local structural rearrangement or decomposition in the oxide layer, and thus that it could promote the transport of the oxidizing species. The non-bridging oxygen atoms are good candidates for such a process because they are less tightly bound; and because the π bonds may act as chromophores and favour local excitation. The growth of the Sb_2O_3 layer at the expense of the Sb_2O_5 molecules and the higher mobility of the oxide molecules on the surface under strong irradiations strongly support this model.

(iv) To be exhaustive we should add the possibility of a thermal dynamic model involving the

opening of fissures and cracks into the oxide layer upon thermal cycling during laser irradiation.

The complete clarification of the driving process requires further experiments. The efficiency of Itoh's mechanism should depend on the absorption of the light into the oxide (dependence on the light energy), on the rate of recombination of the electron-hole pairs into the oxide, and finally on the number of oxygen molecules adsorbed on the surface during the excitation (dependence on the partial pressure of oxygen and on repetition rate).

5. Conclusions

The kinetics of the oxidation of antimony has been found to start very fast and to slow down rapidly because of a lower sticking coefficient of the oxidizing molecules on the oxide. Diffusion along the grain boundaries of polycrystalline samples increase the long term oxidation rate at low temperatures. Under UV excitation, the oxidation is enhanced and the kinetics remains linear. Thick oxide layers can be grown and there are evidences that the oxide layer could be patterned with very good spatial resolution. This low temperature process enables one to achieve very homogeneous nucleation of the oxide layer, and a layer by layer growth. The stoichiometry of the oxide grown under laser light irradiation is poorer in oxygen than the native oxide. A better stability of these oxides is expected in devices, however their aging in atmosphere leads to the superficial saturation of the oxide composition.

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