

## On The Growth Of Native Oxides On Hydrogen-Terminated Silicon Surfaces In Dark And Under Illumination With Light

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After a cleaning procedure, a silicon surface can be terminated by Si-OH groups which results in a high chemical activity. As it is accepted, after removing the wet-chemically grown oxide layer using an HF solution, the surface becomes terminated with Si-H groups. This results in a chemically stable surface (e.g., retarded formation of native oxide). The stability over a period of several hours is reported [1].

Low-temperature processes, including deposition of extremely thin layers, are playing an increasingly important role in modern IC manufacturing. Surface conditions prior to the film deposition can significantly influence interface properties and deposition kinetics. A low temperature results in a limited possibility to activate the surface prior to the deposition. For a stable hydrogen-terminated silicon substrate, the surface activation means reducing its chemical stability caused by the Si-H groups, i.e., desorption of hydrogen from the Si-H bonds.

In this work, we investigated the thickness evolution of native oxides formed on a silicon surface terminated by Si-H groups. Apart from measuring the kinetics of such native oxidation, this should reflect the surface stability over a period of time. The native oxidation in dark was compared with similar oxidation stimulated by the illumination with a 20 W Halogene lamp, having a very low UV emission. To the best of our knowledge, the systematic investigation of the kinetics of the native oxidation of p and n-type silicon, especially concerning the influence of light on this process is very limited. The native oxidation at room temperature was compared with a wet oxidation at 250 °C in an ALD reactor. The oxide thickness was measured at different exposure times to air, varying from several minutes to several days. The oxide growth on both p-type and n-type silicon wafers was compared.

We used (100)-oriented silicon wafers with a resistivity of 2-5  $\Omega$ -cm. All the wafers were subjected to the same cleaning procedure. Cleaning started with a 10-min immersion into fuming HNO<sub>3</sub> at room temperature, followed by a rinse in DI water for several minutes. Then, the wafers were immersed into boiling HNO<sub>3</sub> (60%) for 10 min, followed by a similar rinse in DI water. Further, the wafers suffered from a 30-s dip into a 1% HF solution, resulted in a hydrophobic surface. A 2-min rinse in DI water followed by a 60-s drying using a spinner (both performed in dark) finalized the cleaning process.

The oxide thickness was measured using a modified Kratos XSAM800 XPS apparatus. We used the same model as described in [2] to fit the Si 2p<sub>3/2</sub> peak to different oxidation states of silicon. The quantitative data on oxide thickness were calculated from the peak areas.

In Fig 1, one can observe a noticeable difference in the oxidation rate between the light-illuminated samples and the samples kept in dark. There are two possible explanations of this effect. First, light can enhance

hydrogen desorption, which results in an increased chemical activity of the surface. Second, light generates extra electrons in the silicon bulk. This should enhance the oxidation rate accordingly to the oxidation models proposed in [3, 4, 5]. The model from [5] is based on our recent results on oxidation of silicon in a wet ultra-diluted ambient in the temperature range 750-950 °C [6]. The model considers the electron-stimulated dissociation of the oxidizing molecules. For oxide layers thinner than 2 nm, electrons can tunnel through the growing oxide to the oxide surface. From Fig. 1, there is no measurable difference between the oxidation of p-type Si and n-type Si. From Fig. 2, after a one-day oxidation at 250 °C, the oxide thickness is comparable with the thickness obtained at room temperature under light illumination.

To describe the growth kinetics of native oxides on silicon in a satisfactory manner, we continued developing the oxidation model earlier published in [5]. It appears that the new model is capable of describing the oxidation using a limited number of physically-correct parameters such as reaction rate constants and diffusion coefficients. The model is to be presented in this paper.

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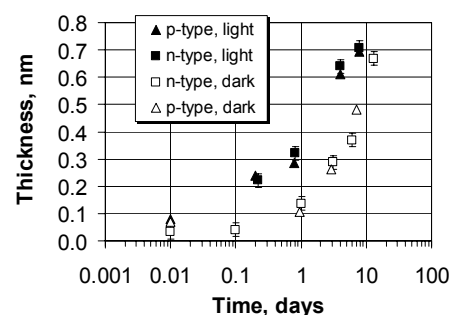


Fig. 1. The native oxide thickness plotted versus oxidation time. The oxides were formed at room temperature in a cleanroom environment (air). Oxidations in dark and under a light source are compared.

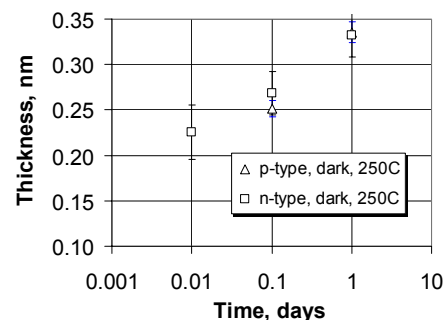


Fig. 2. The wet oxide thickness plotted versus oxidation time. The oxidation was carried out in an ALD reactor at 250 °C and under an H<sub>2</sub>O pressure of 1·10<sup>-3</sup> atm (in dark, no oxygen or dilution with other gases).