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Oxidation of hydrogenated crystalline silicon as an alternative approach for ultrathin SiO_2 growth

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Abstract. This article is devoted to the growth of thin thermal SiO_2 layers on hydrogenated Si substrates as a possibility to obtain improved properties of oxide-Si structure for contemporary MOS devices. Spectral ellipsometry and atomic force microscopy have been applied for characterization of the SiO_2/Si interface and surface morphology. The results show that the oxidation kinetics obeys longer linear time dependence in thin-film regime. The smaller activation energies and higher initial oxide growth rates indicate facilitation of oxide growth in the early oxidation stage. Formation of a reactive less dense Si surface layer is suggested to be responsible for the higher kinetics rates and oxide thicknesses in the very initial stage.

1. Introduction

The major trend in developing metal-oxide-silicon (MOS) devices of new generations is to scale down devices to submicron geometries. That is why the oxidation process in thin film regime has received much attention, but it still remains unexplained with respect to the oxidation mechanism, especially at low temperatures (<900°C). Of particular relevance are a number of studies on the initial oxidation regime, which have implicated the interface reaction as the dominating process for SiO_2 films thinner than 10 nm [1,2]. The pre-oxidation conditions of the Si surface play a decisive role and, hence, will influence the growth kinetics of thin SiO_2 layers and their dielectric properties. Recently we have applied a radio frequency (rf) hydrogen plasma treatment as a Si pre-oxidation cleaning procedure aiming at growth of high quality thin SiO_2 layers at lower oxidation temperatures through incorporation of hydrogen into SiO_2 during the oxidation by hydrogenation of the near surface region of Si [3-5].

In this paper we discuss the low-temperature growth of thermal SiO_2 on (100) and (111) oriented silicon, which underwent standard RCA cleaning and dry rf plasma procedures. Results are presented on the oxidation kinetics and the surface conditions. The SiO_2 growth mechanism is discussed.

2. Experimental details

The substrates were 5-10 Ohm.cm *p*-type (100) and *n*-type (111)-oriented single-crystal Si wafers. The Si oxidation was performed in dry O_2 ambient at temperatures ranging from 800 to 860°C for an

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oxide thickness, obtained from the ellipsometric measurements, ranged of up to 15 nm. Prior to oxidation all substrates were cleaned by standard RCA procedure (clean in H_2SO_4/H_2O_2 solution followed by a dip in diluted HF and rinse in deionized H_2O) and some of the samples were subsequently exposed to a dry hydrogen plasma treatment. The latter is aimed at hydrogenation of the Si near-surface region to alter the oxidation kinetics and was achieved in a planar plasma unit. The rf (13.56 MHz) generator was capacitively coupled to the reactive chamber with an input power of 15 W. The gas pressure was 133 Pa. The substrates were kept at the lower electrode without heating (20°C) or at 100°C for 15 min.

The surface morphology of the samples was studied by atomic force microscopy (AFM) on scanning areas of 1x1 μm with a Nanoscope IIIa, (Digital Instruments). Our previous observations have pointed out that plasma exposure of bare Si leads in general to a surface flattening [6].

3. Results and discussion

According to the widely accepted Deal-Grove model, the kinetics of thermal oxidation of Si follows a linear-parabolic relationship in wide temperature and thickness range [7]. Obviously, here the thin-film regime with linear law is of main concern, since for all samples in the studied thickness range the oxidation kinetics follows a linear time dependence $T_{ox} = At + L_0$, where T_{ox} is being the oxide thickness, A is the oxidation rate constant and L_0 is the extrapolated T_{ox} value of to zero oxidation time. The L_0 value has the physical meaning of initial oxide thickness developed in the very first oxidation stage.

The role of the plasma pre-oxidation treatment is illustrated in figure 1 for (100)Si orientation and it can be summarized as follows. For plasma hydrogenated Si as compared to the RCA wet cleaned Si: (a) the linear kinetics law extends over the whole investigated region (b) the rate of oxidation A is lower (c) L_0 are higher. The oxidation process can be regarded as consistent of surface reaction and diffusion of the oxidant. The linear approximations in figure 1 mean that the oxidation kinetics follows a first order process, which, according to generally accepted Deal&Grove model, is related to surface reaction rate of oxygen and silicon. This process, as often applied to many chemical reactions, can be described by the Arrhenius equation with the intent to infer some insight to the rate limiting process. The oxidation growth rate is described as $A=A_0\exp(-\Delta E/kT)$, where ΔE is the activation energy and A_0 is a temperature independent constant. Here T and k have their usual meanings of the temperature and the Bolzman constant, respectively.

In figure 2 the Arrhenius plots of the oxidation rate for the two Si orientations and different pre-oxidation cleaning conditions are illustrated. The activation energies taken from the straight lines in the plots are summarized in Table I. It can be seen that the activation energies are of the same order of magnitude as those found earlier for dry oxidation in the same temperature range [1,8]. The observed trend is smaller activation energies for the Si substrates cleaned in plasma without heating. The effect of substrate temperature during H_2 plasma exposure on activation energy is to bring it near to the value of RCA cleaned silicon. From these results it can be concluded that the growth of the oxide on hydrogenated Si slows down in the investigated thickness and temperature ranges.

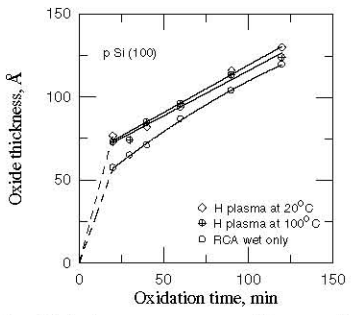

Figure 1. Thickness versus time of (100)Si

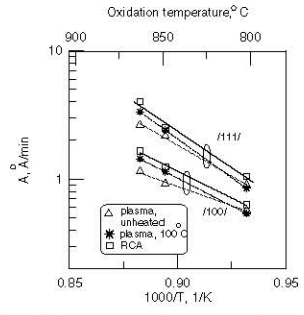

Figure 2. Linear rate constant A versus

oxidation at 800°C.

1000/T for different pre-oxidation cleans.

However, the larger L_o values obtained for plasma cleaned Si indicate higher growth rates in the very first oxidation stages for times below our experimental data points. Moreover, the surface oxidation proceeds faster on (100) Si than on (111)Si. The temperature dependence of L_0 values is shown in figure 3. From this thickness interval additional information about the growth mechanism still can be gained. For quite rough estimation these initial growth rates are evaluated from the slope of the initial linear part, given by dotted lines in figure 1. These lines are linear approximation of the region below the first experimental points assuming zero oxide thickness at the beginning of the oxidation. This latter assumption is not far from reality since hydrogen plasma has already been used to remove native oxide [9]. The oxidation rates A_i characterizing the very initial growth, are illustrated in figure 4.

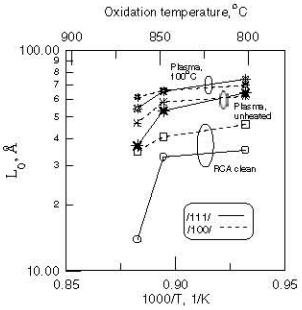

Figure 3. Oxide thickness L_0, extrapolated to zero oxidation time, versus 1000/T.

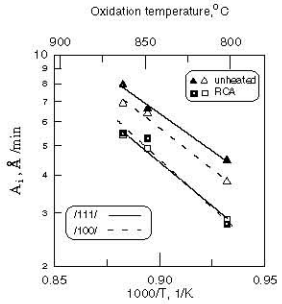

Figure 4. Linear rate constant A_i versus 1000/T for different pre-oxidation cleans.

The experimental data are presented also in Arrhenius plots and the activation energies ΔE_i are given in table 1. The higher ΔE_i value for hydrogen plasma exposed Si indicates facilitation of the oxidation process at the beginning and it is strongly correlated with the observed larger L_0. It has been shown hydrogen plasma creates top surface layer being less dense due to voids decorated with hydrogen [10]. This specific Si layer has to be considered discussing the oxide formation, since the created voids yield more Si sites available for oxidation. The thickness of this specific region depends on the substrate temperature during plasma exposure. Different mechanisms for dry Si oxidation enhancement in the very initial stage have been considered in details [11]. However, in our case the Si surface layer is enriched with hydrogen, which could depress other possible mechanisms and contribute to the observed faster initial kinetics rates A_i and, consequently, the larger L_0.

It is worth to note that the oxidation kinetics changes its law from linear to parabolic when the oxide reaches the unaffected by the hydrogen plasma Si region. Presence of this specific region explains the observed long linear part of the oxidation kinetics and the opposite behavior of the initial stage rate constants of (100)Si and (111)Si orientation [3,12].

Table 1. Activation energies obtained from Arrhenius plots.

Si surface pre-oxidation clean	ΔE (eV)		ΔE_i (eV)	
	(100)Si	(111)Si	(100)Si	(111)Si
RCA wet clean only	1.65	2.25	1.15	1.28
RCA wet and dry H_2 plasma at 20°C	1.18	1.91	1.04	0.98
RCA wet and dry H_2 plasma at 100°C	1.71	2.39	1.04	0.98

The results from AFM imaging have shown that plasma exposure of bare Si leads to a surface flattening although formation of hillocks on the smooth Si surface is also observed [6]. For higher

substrate temperature, larger number of hillocks with larger size has been formed. The lower surface roughness accompanied with hillocks formation is to some extent supporting the suggestion of the presence of a less dense top layer on the Si surface. Because of the thermal oxidation proceeds from surface into Si bulk, the surface nanomorphology follows the state received during pre-oxidation Si treatments but the hillocks formation is enhanced. The latter can be connected with the modified surface region, containing nonuniformly distributed hydrogen inclusions (voids), where the local oxidation proceeds faster. For illustration in figure 5 the three-dimensional AFM images of the (100)Si surface after plasma hydrogenation at 20°C (a) and after subsequent oxidation at 850°C (b) are presented.

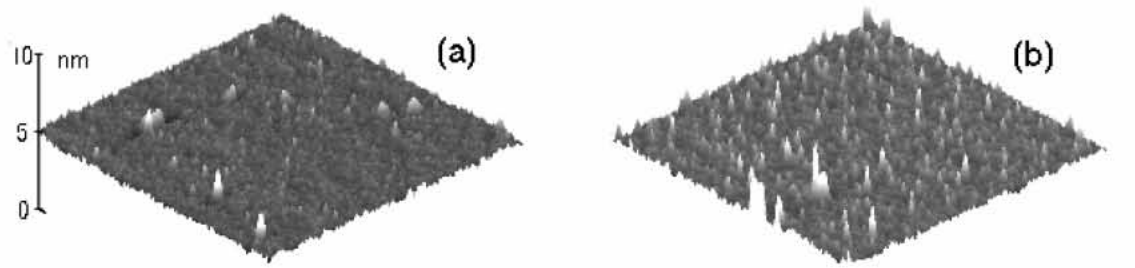

Figure 5. 3D AFM images on a scanning area of 1x1 μm for bare (100)Si wafer after hydrogen plasma exposure at 20°C (a) and after subsequent oxidation at 850°C (b).

The calculated root mean square roughness over the whole areas of the 1x1μm scans showed that hydrogen plasma exposure leads to surface smoothing, while subsequent oxidation increases the surface roughness. All rms roughness values are, however smaller than that produces by RCA cleaning of Si surface. Typical values for a RCA clean are ~0.2 nm [13], close to our observations.

4. Conclusions

It has been established that the oxidation kinetics of plasma hydrogenated c-Si follows a linear law in a considerably large thickness range (up to ~15 nm) with faster initial growth in the very early stage in comparison to the oxidation of RCA cleaned Si. The higher zero time oxide thickness L_0 is supposed to originate from a reactive, less dense layer in the Si, containing voids decorated with hydrogen, formed during hydrogen plasma exposure. The presence of this specific Si surface region explains the observed longer linear part of the oxidation kinetics and the opposite behavior of the initial stage rate constants of (100) Si and (111) Si orientation.

5. References

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