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Distinctive Feature of Thermally Grown Ultra Thin Silicon Nitride Film

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In the current complementary metal oxide semiconductor (CMOS)-CPU generation the silicon gate oxide is 1.2 nm thick. A shrinking of this thickness with one atomic layer for the next generation will lead to a couple of orders of magnitude increase in tunneling current. Another critical issue for future generations is gate oxide degradation due to boron penetration into the oxide from the poly-silicon gate electrode. Ultrathin silicon nitride films have been identified as potential candidates to replace conventional silicon oxide gate dielectrics in current and future complementary metal oxide semiconductor, or as barrier layers between other high-dielectric constant materials and the silicon substrate. We have demonstrated a number of new processes to grow ultra thin silicon oxides and silicon nitrides based on the self limiting nature of the direct interaction between oxygen gas and heated silicon surfaces, or between atomic nitrogen produced in a microwave discharge and heated silicon surfaces. Theses pure ultrathin silicon oxide and nitride films have been studied on Si(100) in ultrahigh vacuum and studied by XPS and high resolution surface sensitive photoemission spectroscopy.

Key Words: Thin film, Nanotransistor, Synchrotron radiation and XPS (X-ray photoemission spectroscopy) techniques.

INTRODUCTION

The microelectronics have entered into the nanometric range due to the continuous shrinking of electronics device dimensions. It is therefore important to study the properties and behaviour of such ultra thin oxide and nitride on Si[1]. But SiO_2 thinner than 1.2 nm may not have the insulating properties required of a gate dielectric. A 1 nm SiO_2 layer is mostly interface (and in silicon bulk), with little if any bulk character. Furthermore, the leakage current imposes a practical limit on oxide thickness[2]. Because for less than 4 nm, the direct tunnelling current increases exponentially by amount one order of magnitude for every 0.2-0.3 nm reduction in oxide thickness[3]. The Si_3N_4/Si films therefore have most effective for the gate dielectrics of next generation[1,3,4].

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The distinctive feature of thermally grown silicon nitride, as compared to silicon oxide is their self-limited growth, which does not depend much on processing parameter and leads therefore to an almost self-controlled thickness. Some other distinctive characteristics of silicon nitride films are: (i) silicon nitride films on Si have a higher density of electronic states as compared to silicon oxide, (ii) the permittivity of Si_3N_4 is about 8, or twice that of SiO_2.Therefore, equivalent oxide thickness (EOT) is large enough for Si_3N_4 films, (iii) silicon oxide has higher mass density, 3.35 g/cm^3 as compared to 2.21 g/cm^3 for silicon oxide[1,2] and (iv) the fact that due to more dense structure and lower density of point defects as compared to silicon dioxide, silicon nitride films constitute more effective diffusion barriers for impurities, not only species like nitrogen and oxygen, but also to fast diffusing species like boron, sodium and even hydrogen[3,4], (v) silicon nitride has a good thermal shock resistance and it retains its high strength and creep resistance at high temperatures[4]. It has been suggested that the thermal Si_3N_4/Si interface is significantly more strained than the thermal SiO_2/Si interface. Nitrogen may lower the interfacial strain and because of free-energy terms the interface is thermodynamically stable. Nitrogen atoms may also compete with boron for occupation of defect sites, so if boron atoms would diffuse substitutionally, a strong Si-N bond would impede substitution of that particular Si atom.

The pure ultrathin silicon oxide and nitride films have been grown and studied on Si(100) in ultrahigh vacuum and studied. The procedure is useful for growing ultra thin nitride films without hydrogen or oxygen impurities and allows us to follow changes in the chemical composition and coordination at the interface, bulk of the nitride and surface of the nitride layer, during growth. The silicon nitride film growth is self limiting, but differing from the self limiting growth of oxide under isothermal conditions, which both have Sigmond-like behaviour.

EXPERIMENTAL

The samples (n-type, 5 Ω cm, 3 cm × 1 cm), were cut out of Si(100) wafers and introduced in the ultra high vacuum (UHV) chamber after a rinse with ethanol in an ultrasonic bath. All further cleaning was done inside the UHV chamber, after baking, by heating the sample with a direct current through it, initially to 1200 ºC, but later, after growth of nitride or oxide films on top, at higher temperatures to restore a clean silicon surface.

In these processes, the oxygen gas was exposed directly on silicon, but nitrogen gas was leaked into a discharge tube connected to the UHV system through a capillary and a 2.5 GHz microwave radiation excited plasma of nitrogen was sent into the reaction chamber through this capillary acting as a differential between the pressure in the excitation region and the UHV. Measurements with a residual gas mass spectrometer has shown that a very high proportion (>50 per cent) of oxygen and nitrogen is produced with this setup. The Si(100) substrate is kept at a stable temperature of 500 ºC or above during the exposure, as measured by an optical pyrometer.

Figs. 1 and 2 show oxidation and nitridation of silicon on Si(100), respectively. Typical total nitrogen pressures in the chamber during exposure were around 5- 5.5 $\times 10^{-7}$ Torr.

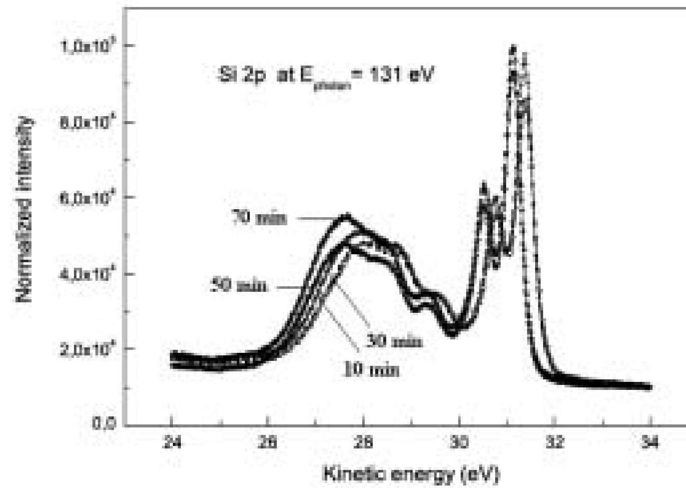

Fig. 1. Si 2p spectra after exposure to 300-2100L (1 L: 10-6 Torr for 1 s) total oxygen at 500 ºC

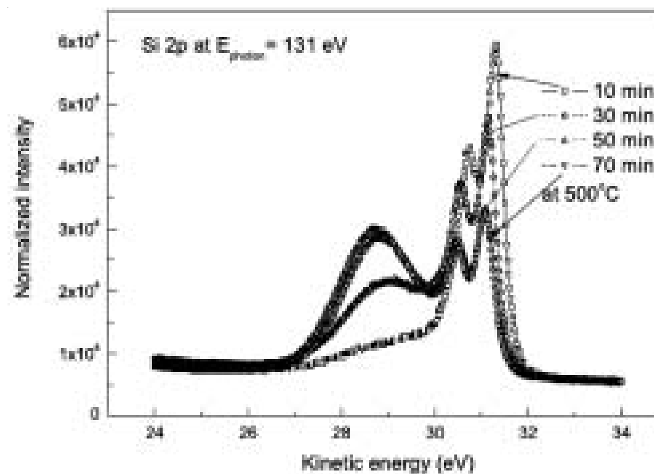

Fig. 2. Si 2p spectra after exposure to 300-2100 L total nitrogen at 500 ºC

These figures show that after the first, short exposure, the bulk Si $2p_{3/2}$ and Si $2p_{1/2}$ peaks are barely reduced in intensity. The following larger exposures change the structure of the entire spectrum. The chemically shifted structures towards higher binding energies compared to the bulk peaks (lower kinetic energies) become more dominating due to the formation oxidation (or nitridation).

RESULTS AND DISCUSSION

These spectra are analyzed in detail by a numerical decomposition, but some of the results are already mentioned here during the presentation of the changes in the spectra.

In addition a new (chemically shifted (about 0.7 eV)) structure is appearing on the low kinetic energy side of the bulk peaks. This experiment, when compared to later experiments, demonstrates that chemisorption with atomic nitrogen initially forms preferentially Si^{3+} and Si^{4+} coordinated surface clusters. The following larger exposures increase the intensity of the shifted part of the spectrum and change the appearance of the bulk peaks considerably.

Each core-level spectrum was analyzed with standard curve-fitting procedures. Using the program FitXPS[5] to decompose the spectra at all steps in spin-orbit split Gaussian-Lorentzian shaped components they were seen to consist of the bulk and four oxide (and nitride) components. For fitting the peaks the following values have been used: Lorentz-full-width-at-half-maximum (LFWHM) = 0.18 eV and spin-orbit splitting = 0.61 eV.

Almost all silicon wafers that are used in microelectronics are single crystalline. Silicon dioxide and nitride, on the other hand, are amorphous. The average distance atoms also differ from one another. Once the silicon surface is oxidized or nitridaized, the interface between these two materials can no longer the perfect. The volume per silicon atom in silicon dioxide (and nitride) is about twice that in silicon crystal, which means that silicon atoms are inevitably emitted from the interface to release stress during oxidation[6] and nitridation. The atomic scale structure of the interface between crystalline silicon and its amorphous nitride is under intense debate, but it is not similar to silicon oxide/silicon interface.

On the silicon side it consists of one or two silicon monolayers in which the atomic arrangement differs from the bulk. Computer simulations of species transport into silicon and the formation of bonds indicate that within the first monolayer there are extra silicon atoms due to stress, before oxygen or nitrogen goes into the silicon network[7,8]. The same simulations provide a partial explanation for the low interface defect densities[7]: during oxidation (and or nitridation) the oxygen atoms can momentarily be bonded to three silicon atoms, which allows the interface to evolve without leaving dangling bonds.

Therefore, as many workers[3,9] suggested there is a transition region, *i.e.*, altered structure and/or stoichiometry with the thickness from 0.5 and 3 nm between crystalline silicon and silicon oxide. This indicates that in the near- interface region there is a zone with excess silicon in the silicon oxide transition region.

All measurements were made at a zero takeoff with respect to the sample surface plane in UHV. From the measured spectra, taken a various times during the growth process, the SiO_2 film thickness, x, is estimated from[10]. The growth mode of the films is revealed in high resolution core level photoemission spectra. When followed

in more detail and converted into thickness, its appearance, as seen in Fig. 3, shows a saturating thickness of oxide about 7-8 Å and that is 2.0-2.5 nm for silicon nitride (Fig. 4).

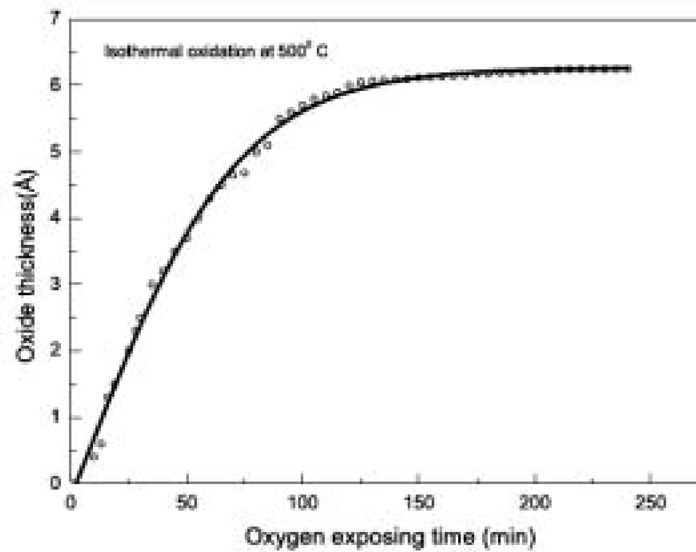

Fig. 3. Saturating growth of a oxide on Si(111)-7 X7 at 500 ºC and $P_{O2} = 8 \times 10^{-7}$ Torr.

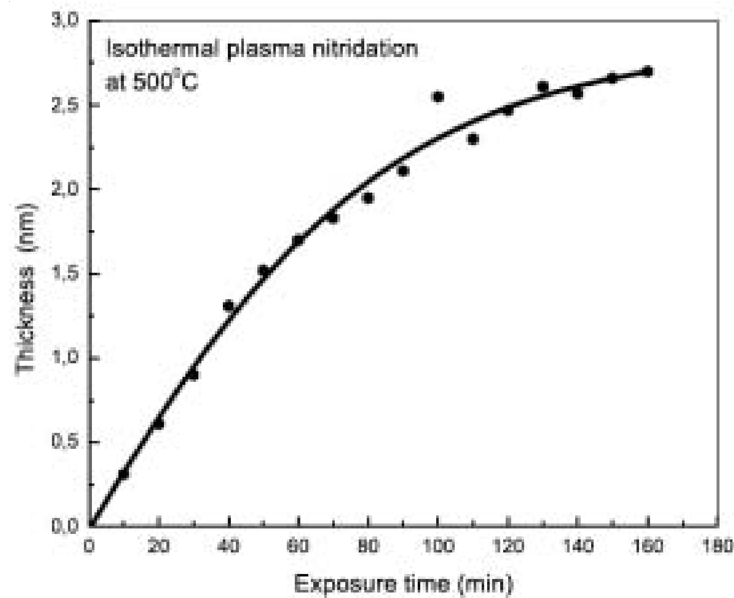

Fig. 4. Saturating growth of a nitride on Si(111)-7 X7 at 500 ºC and PN = 8×10^{-7} Torr.

A saturation of the growth in these processes can be inferred from all of these plots. This thickness could well be a result of the release of strain and stress after growth of a certain thickness of oxide (or nitride), making this oxide (or nitride) impenetrable for further oxygen (or nitrogen), or at least seriously slowing the transport down and into a diffusion, as discussed from a theoretical viewpoint by Demkov *et al.*[6].

One can see that not only the relative intensities of the different film states change, but also the distance from the film/Si interface at which they subsist can be enhanced.

By looking at Figs. 3 and 4, it is clear that the silicon nitride film growth is self limiting, but differing from the self limiting growth of oxide under isothermal conditions. In other words, the above idea shown that mof nitride is followed by a slowing down of the further reaction. This kind of growth kinetics are similar to a growth kinetic behaviour of the isothermal oxidation process with molecular oxygen[10], except for a very significant difference: The self limiting oxide thickness is independent on the temperature[10] and the silicon nitride film growth is not *i.e.*, the limiting nitride thickness varies (increases) with temperature, while for the oxidation it has a maximum thickness at 500 ºC[11].

Based on some fairly simple ideas, to look into the possibility of translating the Deal-Grove mechanism[12] to UHV conditions with special attention to the initially accelerated oxide growth[12], we instead found self limiting creating an approximately 7 Å oxide layer which is in a totally different manner than predicted by Deal-Grove[13]. A behaviour matching this has been suggested from a theoretical simulation of the growth of oxide on Si, containing a ballistic growth phase during oxidation.

Keeping in mind that the fit is only one of a number of fits systematically with a data from all experiments at identical conditions of count rates (noise) and resolution. The only varying physical parameters are the exposure conditions. The fitted parameters include the same widths for all fits and only energies and relative intensities are allowed to vary. However, for the final agreement also some small relative changes of the energy differences between the bulk-Si and the shifted peaks are allowed, based on the understanding of the effect of a varying field in the nitride and oxide which may shift the +3 and +4 peaks originating at the top of thicker nitride and oxide layers. For nitride experiments the systematic changes of intensities of the components are somewhat different as a function of the temperature.

As shown in Figs. 1 and 2, several peaks can be resolved in each spectrum on the higher binding energy side of the bulk Si 2p peak, due to the Si-N and or Si-O bonding[11]. The shift of the bulk peaks typically to lower binding energies with nitride on the surface is indicative of an upward band bending. This indicates that the nitride is negatively charged near the interface[14-20].

Conclusion

Nitrides exhibit several properties superior to those of conventional thermal oxides (SiO_2), the more important being suppression of boron penetration from the

poly-Si. Therefore it has a potential as the gate dielectrics of next generation, because in contrast to SiO_2, silicon nitride films have excellent protective action against diffusion and corrosion.

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