

Ultra Thin Dielectrics for CMOS-Elements

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Abstract: The continued demand for higher density electronic circuits will meet several barriers with the next few years. One of the more obvious ones is the need for reliable method to grow ultra thin dielectric films, such as Al_2O_3 , AlN , TiO_2 , Si_3N_4 and Si_xN_y . Doping of the oxide with nitrogen has been supposed to alleviate both, the tunneling and boron transport issues. Here, we dissolve X-ray photoemission spectrum into Si2p, Si2s, O1s and N1s and find that the influence of N-atoms at the Si (100)/dielectric interface would be detrimental to the electrical properties of devices and the methods were therefore optimized for preventing N-atom diffusion to the interface.

Key words: Nanotransistor • Ultra thin film • Gate dielectric • SiO_2 , Si_xN_y .

INTRODUCTION

In the current CMOS (Complementary Metal-Oxide-Semiconductor) CPU generation from Intel the gate oxide is a 1.2 nm [1-5]. Thick layer of SiO_2 doped with nitrogen. This configuration suffers from relatively large leakage currents and a further shrinking of the thickness would lead to a further increase of the tunneling current by a couple of orders of magnitude for each “atomic” layer removed [5-10]. However, such a thin gate dielectric is required to improve the drain-current response of Nano transistor to the applied gate voltage (allowing low voltage)[10-18].

On the other hand, the work of Muller *et al.* [19] from Lucent Technology is an experimental proof of the fundamental physical limit to the size of a working gate oxide. Using an electron microscope in combination with spectroscopic analysis of the electron energy in the Si/ SiO_2 interface, they show that electronic wave functions penetrate from the ultra thin oxide film from both interfaces. This means that another critical issue is gate oxide degradation due to boron penetration into the oxide from the poly-silicon gate electrode.

Doping of the oxide with nitrogen has been supposed to alleviate both, the tunneling and boron transport issues. Therefore, we could find an alternative to SiO_2 which is silicon Oxynitride due to its higher dielectric constants, its amorphous structure and higher EOT (Equivalent Oxide Thickness).

Analysis of X-ray Photoemission Spectroscopy: Two-inch boron doped (100) silicon wafers ($N = 0.5 - 10 \times 10^{16} \text{cm}^{-3}$) were used as substrates. These were thermally dry oxidized at 1100 °C to form a 20 nm thick insulator layer at high pressure, but for growing thin and ultra thin oxide, Silicon were oxidized at ultra high vacuum (UHV) conditions and (at 500 °C). At UHV conditions, the maximum thickness of the silicon oxynitride film (2.5 nm) could be formed on the Si (100) substrate (Fig.1).

The curve in Fig.1. indicates nearly identical growth of film at 500 °C. The film thicknesses derived from X-ray photoemission with the equation [20].

$$\frac{I(\text{O}1s)}{I(\text{Si}2p)} = \frac{I(\text{O}1s(\text{SiO}_2))}{I(\text{Si}2p(\text{Si}))} \cdot \frac{1 - \exp\left(\frac{-x}{21.4\text{\AA}}\right)}{\exp\left(\frac{-x}{26.7\text{\AA}}\right)} \quad (1)$$

And

$$\frac{I(\text{N}1s)}{I(\text{Si}2p)} = \frac{I(\text{N}1s(\text{Si}_3\text{N}_4))}{I(\text{Si}2p(\text{Si}))} \cdot \frac{1 - \exp\left(\frac{-x}{21.3\text{\AA}}\right)}{\exp\left(\frac{-x}{26.7\text{\AA}}\right)} \quad (2)$$

Where I stands for XPS peak intensity and the other numbers in nm indicates the sampling depths of the O1s, N1s and Si2p lines with a Mg X-ray anode found with Morgen and Bahari [21].

We show two XPS Spectra (10 and 20 min exposure time) of the silicon oxynitride film on the silicon substrate in Fig.2.

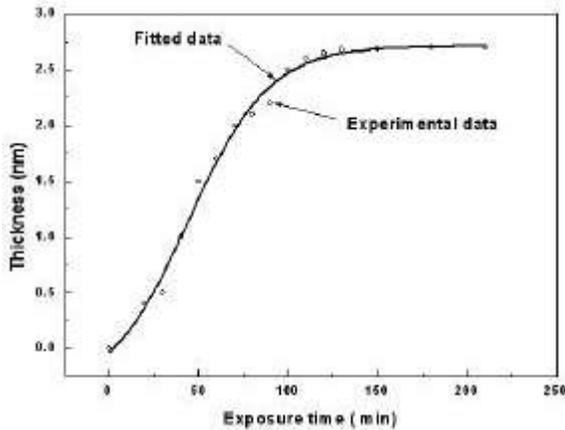


Fig. 1: Growth of silicon oxynitride during isothermal oxynitridation with plasma dissociated nitrogen (N- atoms)

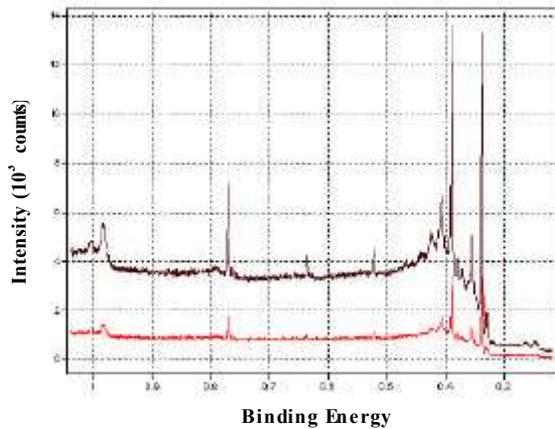


Fig. 2: XPS spectra of SiO_xN_y on Si (100) at 600 °C (Nitrogen exposing time: 10 and 20 min).

We could grow the thick oxide film at high pressure (1 atm) and high temperature (1020 °C). The thick nitride film was formed on silicon substrate at high pressure (1 atm) and high temperature (900 °C) with using NH₃ gas. Therefore, we found:

$$\frac{I(O1s)}{I(Si2p(Si))} = 0.5 \quad \text{and} \quad \frac{I(N1s(Si_3N_4))}{I(Si2p(Si))} = 3.5 \quad (3)$$

With using above data and O1s, N1s and Si2p peaks in XPS spectra, we estimated the thickness of oxynitride film, as shown in Fig.1. It is seen that the growth of the film is self-limiting and the kinetics are found to follow a (half) sigmoid functional:

$$Y = a + \frac{b}{1 + e^{x_{50\%} - x}} \quad (4)$$

Where a is the start value, b is the limiting (saturating) value, x_{50%} is the value where Y has reached half of its maximum value and b is a parametric determining the steepness.

DISCUSSION

As mentioned above, the growth of the oxynitride film on the silicon substrate is self-limiting growth. This behavior is radically different from those of the Deal-Grove / Massoud et al. models [22-23]. These results [2-5] were completely surprising in two ways: No previous reports exist about this self-limiting oxynitridation process for Si despite simplicity of the experiments and our previous works [1-8] indicate.

Limiting thickness obtained is almost independent of the temperature in the regime covered here. We can extract more information about the chemical bonding of Si in the sampled volume from with looking at the core level Si2p spectra. It includes the effects of band bending which is a function of charges in the oxynitride layers and can serve as a monitor of these effects.

We guess the surface state density of these MOS structure to be quite good and is slightly above $10^{11} \frac{e}{V.cm^2}$

in the mid-gap. An increase in surface state densities can be around 0.7 eV above the valance band. This might be caused by the impurity energy levels of oxygen, nitrogen and silicon ions. Broken Si-O, Si-N, O-Si-N and Si-O-N caused among other things by annealing, can be in the appearance of a localized peak of interface states at 0.8 eV.

The dangling bands tend to form a peak at 0.3 eV above the valance band [22]. However, the situation improves significantly when the layer thickness increases to 3nm. Because of the fabrication method used at [22], the Si/SiO_xN_y interface should always be similar regardless of the layer thickness. At room temperature it is unlikely that there will be many changes in the interface structure because of oxygen and/or nitrogen diffusion or strain when new oxynitride layers are added to the structure. This phenomenon may also be caused by impurities from the boron atoms which tend to decrease with increasing oxynitride thickness.

CONCLUSION

Various thermal oxidation and nitridation methods have proven to be accurate, reliable and to produce an extremely high film quality. Nonetheless there do remain other purposes for our work. For this purpose the spectra are carefully analyzed and studied because the interface quality is even better than oxide dielectric in MOSFETs. The oxynitride film growth is self-limiting and can be used as a new and good gate dielectric for the next Nano transistor generations.

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