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Nitridation of SiO₂ for Surface Passivation

Stefan K-C Lai
Intel Corp., 3065 Bowers Ave.,
Santa Clara, CA 95051

I. INTRODUCTION

Thermal silicon dioxide has been one of the most important insulator for the present microelectronic technology. Not only is it an almost perfect insulator, its interface with silicon is very close to ideal, giving the lowest density of electrically active interface traps. Active transistors can only be fabricated successfully because of the low density of electronic traps. Furthermore, the low density of interface traps also provides an ideal passivation for the silicon surface electrically.

Silicon dioxide, however, is not perfect. The oxide network is actually a very porous network, allowing the diffusion of gaseous species through it, especially at elevated temperatures. This can change the electrical and thus the passivation properties of the oxide. Also, the oxide network can be very easily damaged by energetic particles and high energy radiation. This damage gives rise to an increased density of electronic states, both in the bulk of the oxide and at the silicon-silicon dioxide interface. The sum of the above effects is a long term degradation of the oxide and its interface with silicon, especially in the space environment.

Besides the above factors, there is a third factor that provides the driving force in the search for a better insulator: the defect density of silicon dioxide increases with decreasing oxide thicknesses. With the scaling of device dimensions in the quest for the highest packing density in integrated circuits, the vertical dimensions are also scaled. It is expected that 10nm oxides will be used extensively in half micron devices by the end of this decade. The yield and reliability of the present oxide system may not be able to satisfy the requirement.

It was under these conditions that Ito et al set out to develop a better insulator for silicon. They first reported the direct nitridation process to form a thermal nitride (1). However, such processes require very high temperatures and long process times. The nitrides formed were only of limited thicknesses (up to 5nm) and rich in oxygen (1,2). The films obtained are believed to be basically oxynitride layers. Next, they reported on the nitridation of silicon dioxide, which is the subject of this paper (3,4).

II. NITRIDATION OF SILICON DIOXIDE

Experiments on the nitridation of silicon dioxide has been reported many times in the literature (5). Ito et al first reported the thermal nitridation of silicon dioxide in ammonia (3). They reported that nitridation retarded the

destructive breakdown of silicon dioxide films (4). They explained the effect by the fact that the current through the oxide was much more uniform. They had also reported in detail the MOS characteristics of silicon dioxide nitrated under different conditions (6). Since then, it has been reported that nitrated oxide was effective in reducing the diffusion of boron through the dielectric, compared to the case of pure oxide (7). Terry et al reported on the radiation effects in nitrated oxide (8). They observed that there was very little generation of interface traps after radiation damage.

There have also been many papers published on the material characterization of the nitrated oxide (5). The common observation was that after nitridation, the dielectric was a very effective barrier to the diffusion of oxygen and water: it demonstrated very high oxidation resistance. This is consistent with the observation that it is an effective boron diffusion barrier. Auger experiments showed that there was a build up of nitrogen close to the silicon-silicon dioxide interface, resulting in a layer that was difficult to etch chemically and was probably the major barrier layer (9). Recently, more detail XPS (X-ray Photoelectron Spectroscopy) experiments showed that the nitrogen layer was located at a small distance (2.5nm) away from the interface (10). In general, the results were not completely consistent, which was probably due to the fact the process control was very difficult. Trace amount of oxygen or other impurities can change the reaction kinetics. The process history of the film may also affect the material characteristics.

In the present paper, an attempt will be made to relate the electrical properties of the film to the process history. A model is proposed to explain some of the observed results. It will be shown that with our present knowledge of the dielectric, it shows a lot of promise for its use in surface passivation, both for its resistance to impurity diffusion and for its resistance to radiation damage effects.

III. ELECTRON TRAPPING

Electron trapping can be used as a sensitive probe to the impurities and defects in silicon dioxide or related insulators and their interfaces with silicon. Generally, electron traps can be divided into two categories: intrinsic traps and high field generated traps (11). Intrinsic traps are traps that are present in the oxide after processing, either as impurities such as arsenic (12) or water related centers (13), or due to high energy processing such as plasma etching (14). The plasma or other high energy radiation give rise to hole trapping close to the interface and neutral electron traps in the bulk of the oxide. The electron traps can be filled by low field electron trapping experiments, most conveniently the injection of electrons by RF avalanche processes in silicon (13). Each kind of electron traps have their characteristic capture cross section which can act as a signature to their origin (11). The trapping process also follows classical trapping kinetics: the traps are filled over time, and the flatband voltage shift due to electron trapping will saturate.

When an oxide is subjected to high current and high electric field under the Fowler Nordheim tunneling condition, additional electron traps are actually generated by the process (15). In this case, the flatband voltage

does not saturate but will continue to increase with increasing electron fluence, until final breakdown due to the build up of a very high internal electric field due to the high density of trapped electron (16). The high field trap generation process is very similar to radiation damage. They both give rise to positive charge at the interface and the interface traps in both cases show a characteristic peak above midgap close to the conduction band (17). An increase in electron traps is observed in the bulk of the oxide, similar to the generation of neutral traps (11).

The change in the density of low field electron traps after the nitridation process was studied (18). In the experiment, oxides were annealed in ammonia at different temperatures for different times, with the results for one temperature shown in Figure 1. It can be seen after the nitridation process, there was a large increase in electron trapping at low electron fluence. When the trapping curves were analyzed, it was concluded that the increase in trapping was due to an electron trap with capture cross section of 10^{-17} cm². Nitridation at higher temperatures and longer times gave the same electron trap with the same capture cross section. However, the saturation density was slightly different, with slight increases for higher temperatures and longer times. This electron trap has been identified as due to OH centers in the oxide. This was confirmed when it was shown that from infrared absorption spectroscopy, an increase in density of OH bonds similar in density to the electron traps was observed. It was postulated that in the nitridation reaction, oxygen might be released from the oxide and reacted with the hydrogen in ammonia to give rise to the OH bonds.

The trapping process under high electric field for Fowler Nordheim tunneling in thin dielectric was then studied. The experiment involved the passing of constant current through the dielectric. Any electron trapping would increase the voltage required for the same current. Thus, the change in gate voltage is a measure of electron trapping. The trapping curve for the oxide in Figure 2 is characteristic of high field trapping process: there was an initial decrease in gate voltage due to the generation of holes, which actually enhanced the injection of electron. After about ten seconds, the curve changed in direction and there was a continuous increase in voltage shift due to the generation of additional electron traps. This is to be contrasted with the classical picture where the curve would saturate when all the traps are filled. For the nitrated oxide (NO), there was little or no hole trapping and the increase in electron trapping was faster compared to an oxide. The dielectric actually broke down in a short time because of the high internal field. The third sample called ONO (oxidized nitrated oxide) showed little hole trapping as well as little electron trapping. Electrically, this seems to be the most stable dielectric for the three studied. The lack of electron trapping in ONO was confirmed when it was shown that there was no window closing after extended cycles in E²PROMs (19). Other experiments in E²PROM had shown that there was hardly any hole trapping for ONO.

The properties of the dielectrics were studied further by subjecting the samples to high temperature anneal in an inert atmosphere (Nitrogen). The results were shown in Figure 3. For the oxide, the trapping process was increased slightly, but with the same characteristic features. The most dramatic change was observed in the nitrated oxide (NO). The density of electron traps was reduced to very low levels, similar to ONO before anneal. For ONO, there was actually a slight increase in trapping.

The above results is for a given nitridation condition. When the nitridation time is reduced by half, different results were obtained. For NO, the initial electron trapping was reduced. On the other hand, after the high temperature anneal, the electron trapping was only partially reduced. The results seemed to indicate that the dielectric is a mix between oxide and nitrided oxide. It is very important to realize that different process conditions affect the trapping properties significantly. The degree of nitridation initially and the post nitridation thermal cycle both change the dielectric characteristic. Furthermore, the nitridation conditions used in the present experiments are typically much more gentle compared to those reported in literature because the films were intended to be used in state of the art VLSI processes. Different results may be obtained for those heavily nitrided films.

To understand the experiments better, quasi-static capacitance curves (QCV) were obtained for the samples before and after different amount of electron fluence. Any interface trap generation will give distortion in the QCV curves while bulk trapping will give horizontal shift in the curves. The interface trap generation process was very similar to the bulk electron trapping process. The results are shown in Figure 4. For an oxide, after the high electron fluence, there was increasing distortion in the QCV curve. There was also a characteristic structure in the curve which was due to an interface trap peak. Similar peaks were observed in oxides damaged by radiation. This strongly links the present high field damage process to the radiation damage process. For the unannealed NO, little or no distortion in the QCV curve was observed. Instead, an almost parallel shift in the curve was observed. It can then be concluded that there was no generation of interface traps, and there was high density of electron traps in the bulk of the dielectric. Finally, for ONO and also annealed NO_2 , there was little or no change in the CV curves after up to two coulombs/cm².

IV. MODEL

The above results can be explained by a very simple model. For an oxide, the electron trapping was due to high field generated traps. For the nitrided oxide with no anneal, there was more electron trapping which can be explained by the increase in OH centers shown in Figure 1. The only question is: what happened in the case of ONO? The effect can be explained by assuming that after nitridation, the density of high field generated traps were reduced to very low levels. This is supported by the results of the QCV experiment: there was no generation of interface traps, which are related to high field generated traps in the bulk of the oxide. Then, for ONO, the extra anneal reduces the density of OH to very low levels. This reduction after anneal has been reported before (20). With no OH sites and no high field generated traps, there is very little electron trapping. Oxygen is not required to reduce the density of electron traps. When the nitrided oxide was annealed in nitrogen, the lowest density of electron traps were obtained.

For a pure oxide, the high temperature anneal actually has an opposite effect on trap generation. Such an anneal has been shown to increase positive charge trapping and interface trap generation after radiation damage (21). In Figure 3, the high field trap generation in oxide was increased after the high temperature anneal. For ONO, the oxidation could have increased the oxide

properties such that after anneal, the rate of electron trapping was also increased.

The same model can be used to explain the observation at the silicon-dielectric interface. The nitridation process changes the interface such that it is no longer susceptible to high field damage. Recently, the detail of the interface damage process at the interface was studied (22). It was shown that the characteristic interface peak was not generated when holes were first trapped at the interface. Only when an electron was captured by the hole that the interface trap peak was observed. A model based on strained bonds at the interface was used satisfactorily to explain the observation. It was also proposed that the model can be used to explain radiation damage and neutral trap generation in the bulk of the oxide. From the present experimental results, the high field trap generation process can also be explained by the same model. In the simplest term, the damage process under high electric field and high energy radiation have similar origin.

The present results thus show that nitridation modifies the oxide network in a major way. It can be postulated that the nitrogen may go in and replace the strained bonds selectively, forming a silicon-nitrogen structure which may be much more stable. Possibly, the bonds are no longer "strained" and when holes are captured at the sites, the bonds do not go through a relaxation process. On capture of electrons, the bonds will return to their original state and no permanent damage states are generated.

For samples which were not nitrided for as long a time, there will be a lower density of OH traps. Also, the reduction of strained bonds by nitridation will also be limited. After the OH sites are reduced by an anneal process, the remaining strained bonds can give rise to significant electron trapping under high field conditions.

The reduction of OH bonds through anneal is basically a diffusion process. The thickness of oxide and the annealed temperature thus play a very important part in determining the final density of OH sites in the dielectric. The above experiments were carried out in oxides in the 10nm range because the dielectric was intended to be used in E^2 PROMs. In this thickness range, it was shown above that it is possible to reduce the OH sites to very low levels. However, it is also important to remember that after the nitridation process, the dielectric is a very effective diffusion barrier. It would not be surprising that for thicker nitrided oxide, it would be much more difficult to reduce the OH sites, giving rise to a high density of bulk electron traps. This may explain some of the inconsistency that may have been observed.

V. DISCUSSION

There are two properties of the nitrided oxide discussed above that make it promising as a new dielectric for surface passivation. Firstly, the dielectric is a very good diffusion barrier. It gives the surface much better protection to the possibility of degradation from impurity elements. Secondly, from the results presented above, it appears that the dielectric is also very stable electrically. Specifically, the silicon-dielectric interface may not be degraded in a radiation environment. The use of the dielectric thus provides potentially a very stable passivation for silicon.

The present work has been only limited in scope, even though it shed a lot of light on the electrical properties as related to the chemistry of the system. No attempt had been made to study the detail of all the process conditions and correlate to radiation damage experiments. It is important to study the whole system in a comprehensive and detail manner in order to realize the full potential of the system.

VI. ACKNOWLEDGEMENT

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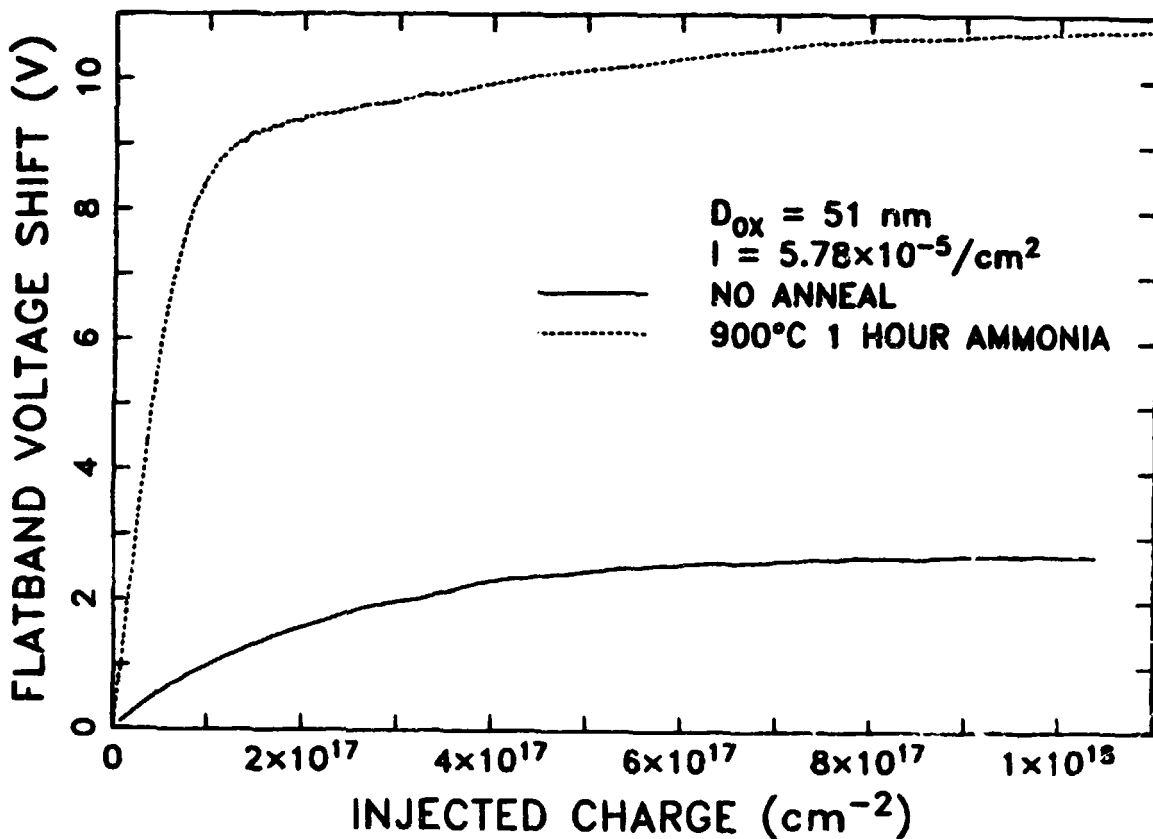


Figure 1: Flatband voltage shift as a function of injected electrons for a 51nm oxide with and without the ammonia anneal. The large increase initially for the annealed sample was due to a new electron trap with capture cross section of $10^{-17} / \text{cm}^2$.

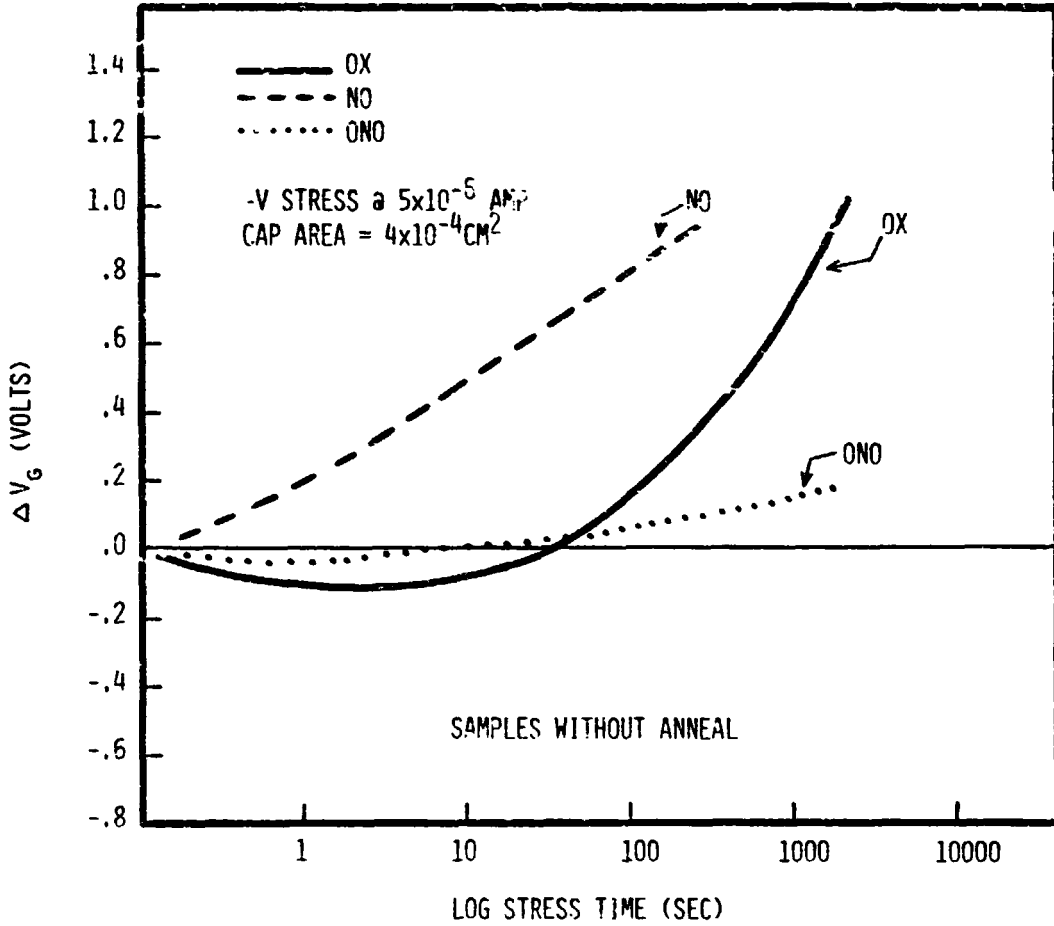


Figure 2: The change in voltages across oxide, NO and ONO capacitors under constant current as a function of Log time. This is a measure of electron trapping which results in the shifts of IV curves under Fowler Nordheim injection.

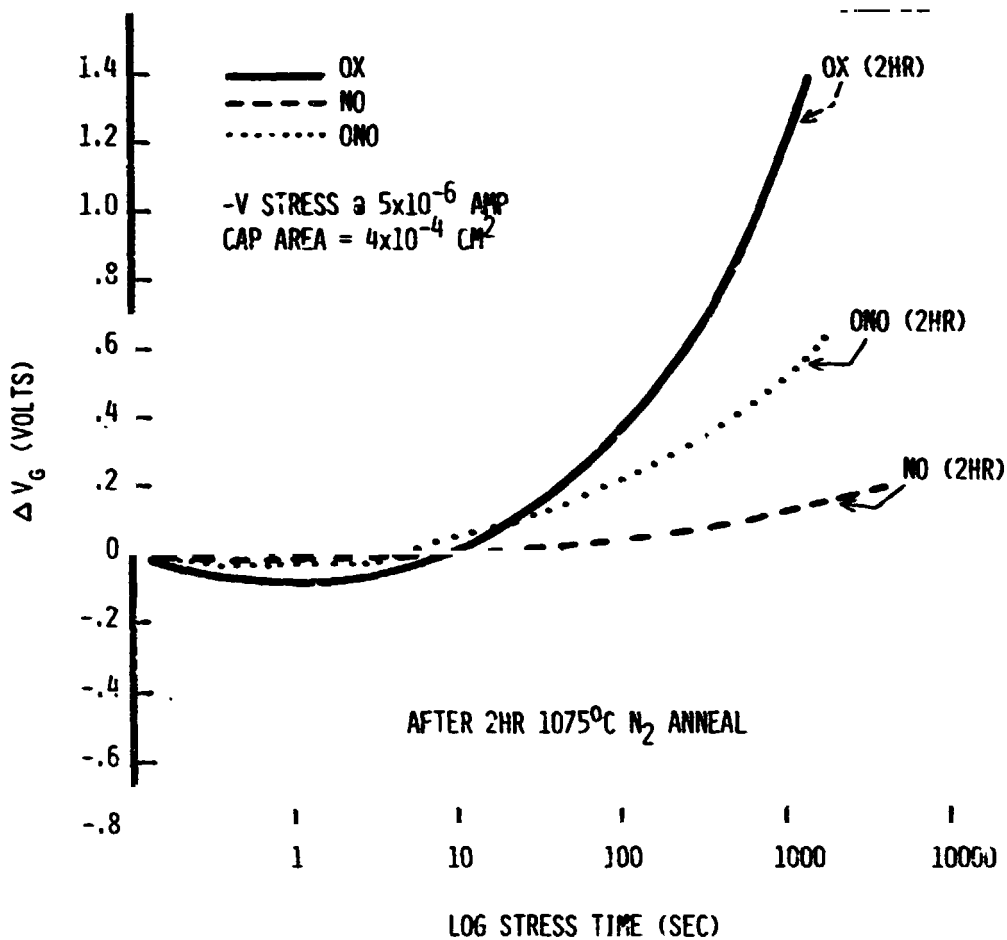


Figure 3: The changes in voltages across oxide, NO and ONO capacitors under constant current as a function of Log time. The samples were annealed for 2 hours at 1075°C in nitrogen.

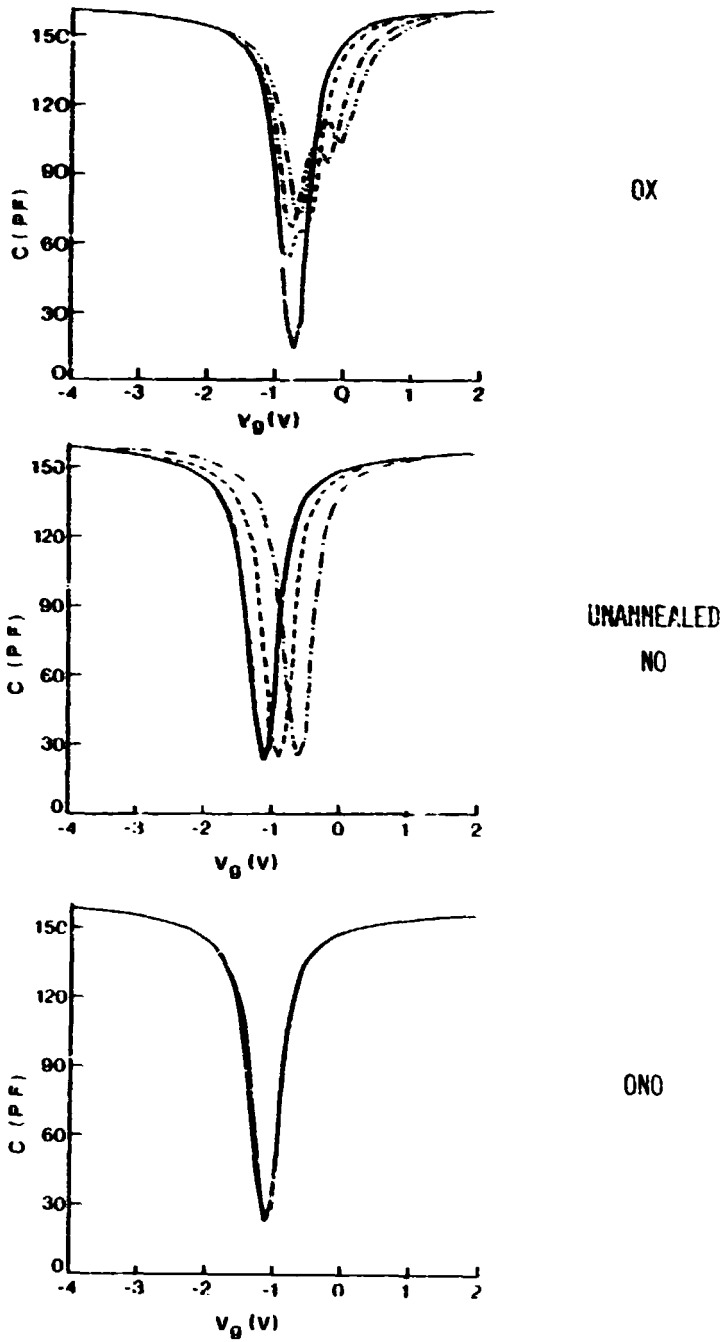


Figure 4: Quasi-static capacitance curves for an oxide, NO and ONO. The family of capacitance curves in each plot was due to increasing stresses across the dielectrics₂ under constant current. The stress was approximately 0.5 coulombs/cm² per step.

DISCUSSION

ROHATGI: I can see that nitrided oxides are very good for VLSI, but from the point of your solar cells, they may not work because most of the nitrided oxides have been fabricated at temperatures of around 1100°C to 1200°C.

LAI: Well, I can tell you that for our purposes, for our work, we look at nitration conditions, which is consistent with VLSI processing. The conditions that I have shown you, up until now, in detail, there is no inconsistency at all with VLSI processing.

ROHATGI: That is what I am trying to point out, it is very good for VLSI because it takes care of radiation problems.

LAI: By VLSI, I mean that we are going away from high-temperature processes altogether. I don't see the nitration condition we have used is much lighter, compared with everything that is reported in the literature.

ROHATGI: I have made some nitrated oxide for passivating solar cells. Our solar-cell junctions have to be very thin, also, so I stayed at temperatures around 850°C. So I grew 100 Å oxide nitrided in ammonia at 850, and there was no real difference in the passivating properties of the oxide I had and the nitrided oxide. Then I went to a thermal nitride without any oxide, trying to make an MIS contact, and that was even worse. So it looks like if you are going to use this nitrided approach you have to figure out a way of doing it at low temperatures, because you don't see all these beneficial effects.

LAI: Well, I guess the important thing is, what properties you look at for passivation. I will have to calibrate it to the point of data I have here. Have you looked at interface properties, CV curves, at bonded or impurity diffusion, those kinds of conditions?

ROHATGI: I think interface properties is the key here, because that is what determines the surface recombination velocity, and like you said, unless you do the nitridation at temperatures 900 or above, you don't see all the good effects that have been reported in literature.

LAI: That is what I said earlier, though. I don't think my experience has been that it does not really improve the surface. But all I have stated here is more for long-term reliability, and it is a much more stable system, which I think is a very important thing, at least for our process.

GRUNTHANER: I think the dielectric material that you are looking at with the nitrided oxide shows a lot of really exciting possibilities, particularly in terms of generation mechanisms of more excited states. But there is one piece of information that you may or may not be aware of that has come out of the Hewlett-Packard studies, which I think may have some severe impact on the solar cell situation here. That is, the experiments looking at the lattice imaging of the silicon surface, comparing thin SiO₂ films with these nitrided oxides. The interesting thing about

those results is that the surface of the silicon itself at the very abrupt determination, the last three or four atomic layers of the silicon, has significantly relaxed. There is much less strain at that surface situation, as you can see from the lattice-imaging TEM micrographs, and I think there are some very serious implications for some of these recombination losses and so on in that. I don't know what they will turn out to be but I think --

LAI: Well, is that good or bad, though?

GRUNTHAMER: That's right. I don't know which way it is going to go, but there clearly is a difference, and I think the first difference that has really been seen is in these dielectric films that have been grown. A variety of other approaches have been taken, but always very similar reconstruction strains, and so on, on the surface of the silicon. Yet only in this nitrided oxide are they seeing an actual relaxation of the top surface there for such sharp and coherent planes.

RAO: In those annealing experiments -- this is just a takeoff on his question -- what happens when you use, say, an inert gas like argon at the same temperature instead of nitrogen? Have you had any results on that?

LAI: No. I have not done the experiment.