Nature of the dominant deep trap in amorphous silicon nitride

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We observe a strong correlation between changes in the density of paramagnetic silicon-"dangling-bond" centers and changes in the space-charge density in amorphous silicon nitride films subjected alternately to positive and negative charge injection and optical illumination. Our results provide, for the first time, direct experimental evidence associating a specific point defect with the trapping phenomena in amorphous silicon nitride. We also demonstrate both directly and for the first time the amphoteric nature of the silicon nitride silicon-dangling-bond center.

The importance of silicon nitride (Si_3N_4) in microelectronic devices is well established. This insulator is used in a variety of devices, such as insulated gate field-effect transistors (IGFET's),[1] metal-nitride-oxide-semiconductor (MNOS) nonvolatile memory devices,[2] and amorphous hydrogenated silicon (a-Si:H) thin-film transistors.[3] It is also utilized in metal-insulator-semiconductor solar cells[4] and has long been used as a passivating layer in silicon—silicon dioxide structures. It is well established that the electronic properties of silicon nitride films are dominated by the presence of deep trapping centers.[5-8] These trapping centers play a critical role in silicon nitride films used in nonvolatile memories,[9,10] and may seriously limit the usefulness of this dielectric in IGFET's[11] and a-Si:H thin-film transistors.[12] The electronic properties of these centers have been studied intensively over the past decade[5-10,12-20] and numerous models have been proposed characterizing their behavior.[9,10,13-15] However, no direct experimental evidence has been presented in which a specific structural defect is directly linked to a deep trapping center.

Recent experimental and theoretical studies have explored the origin and charge state of traps associated with amorphous silicon nitride films used in nonvolatile memory devices.[9,10,13-15] Several very different models have been proposed by various authors explaining charge trapping behavior in these films. Kirk[14] has suggested that nitrogen dangling bonds are responsible for charge trapping in MNOS devices. On the other hand, Robertson and Powell[13] and Ngai and Hsia[9] have argued that a silicon dangling bond is responsible for charge trapping in silicon nitride. Kapoor *et al.*[15] have proposed that silicon–hydrogen bonds are the source of memory behavior in silicon nitride. However, until now there has been no direct experimental evidence linking any of these defects to a trap center in the nitride.

Electron-spin resonance (ESR) has been a very useful method for identifying the roles that trapping centers play in the electronic properties of amorphous silicon[21]

and amorphous silicon dioxide.[22,23] Several recent ESR studies[10,16-20] have shown that paramagnetic dangling-bond centers are present in amorphous silicon nitride films. In stoichiometric nitrides it has been argued that these centers are silicon atoms bonded to three nitrogen atoms.[25] In this article, we use electron-spin resonance (in conjunction with electrical and optical techniques) to explore the electronic properties of silicon-dangling-bond centers in amorphous silicon nitride.

We report results of an experimental study in which we inject positive and negative charge into amorphous (stoichiometric) silicon nitride films. We use ESR to monitor the density of silicon-dangling-bond centers, and electrical (capacitance versus voltage) measurements to calculate the density of trapped charge. We find that the capture of either positive or negative charge by trapping centers in the nitride is consistently accompanied by an approximately equal decrease in the density of paramagnetic silicon-dangling-bond centers. We also find that ultraviolet (uv) illumination of charged nitrides annihilates the space charge and that this disappearance of trapped charge is accompanied by an approximately equal increase in the number of paramagnetic silicon-dangling-bond centers. Our observations provide the first experimental evidence directly identifying a specific structural defect with the dominant deep trapping levels in amorphous silicon nitride. We also provide the first direct experimental evidence that the amorphous silicon-nitride-dangling-bond center is an amphoteric defect.

The silicon nitride samples used in this study were deposited via low-pressure chemical vapor deposition at 760 °C to a thickness of 5500 Å. Sample substrates consisted of lightly doped (5×10^{14} cm^{-3}), $\langle 111 \rangle$-oriented crystalline silicon wafers on which a 250-Å thermal oxide had been previously grown. A 200–300-Å thermal oxide layer eliminates charge injection in our nitride films at moderate electric fields, and makes our electrical [capacitance-voltage (CV)] measurements reliable. However, at high fields this layer is thin enough to permit tun-

neling of carriers through the oxide. The nitride films were stoichiometric with an optical band gap larger than 5.5 eV, and contained less than 2 at. % H. ESR measurements were conducted at room temperature on an IBM Instruments ER-200 X-band spectrometer. A TE_{104} "double" resonant cavity was used with a calibrated weak pitch spin standard so that accurate determinations of both the relative and absolute number of spins could be obtained. Our ESR measurements were consistently repeated to better than $\pm 5\%$ and we estimate that our relative spin concentration measurements are accurate to better than $\pm 10\%$. We estimate that our absolute spin concentration measurements are accurate to better than a factor of 2. When making ESR measurements, care was taken to avoid microwave cavity loading or saturation effects.

CV measurements allowed us to determine the density of space charge in the insulating films.[25] The density of space charge was determined from shifts in the high-frequency (1-MHz) CV curve taken at the point where the interface Fermi level is in the middle of the silicon band gap V_{mg}, the midgap voltage. We estimate the accuracy of our space-charge determination to be $\pm 10\%$. Ultraviolet illumination was provided by a 100-W Oriel mercury light source and a 4.9-eV (254-nm) bandpass filter; the light intensity from this source-filter combination was roughly $1~\mu W\,cm^{-2}$. Biasing was performed by depositing low-energy ions created by a corona discharge apparatus onto the samples.[26] These ions have essentially thermal kinetic energies and thus do not damage the surface of the nitride films.[26] The corona discharge technique can produce relatively large (> 7 MV/cm) uniform electric fields over a large surface area (1 cm^2) without destructive breakdown.[26] This technique also allows us to selectively charge the nitride films with positive or negative space charge. Different samples were used in the experiment for ESR and CV measurements; however, ESR and CV samples were always taken from the same location on the same wafer, and care was taken to expose them to precisely the same conditions throughout the experiment. (Essentially identical results were obtained on numerous samples.)

It has been shown previously[27] that subband-gap uv illumination creates stable paramagnetic defects in amorphous silicon nitride. By performing an etchback study on an illuminated silicon nitride films, we have found these paramagnetic defects to be roughly uniformly distributed throughout the bulk of the silicon nitride. We have also observed from CV measurements that uv illumination eliminates any charge previously trapped in the nitride films [Figs. 1(a), 1(c), and 1(e)]. uv illumination thus allows us a reference point in our experiment. In other words, we can repeatedly cycle the samples through a series of charging conditions, always returning to our starting conditions with the use of a uv source.

Initially, the silicon nitride films were illuminated via the uv source for 20 min. This resulted in a large increase in the number of paramagnetic defects in our samples (3.6×10^{13} spins/cm^2) and annihilated any net space charge previously in the samples [Fig. 1(a)]. Next, the samples were subjected to a positive bias (with respect to

the Si substrate) via (positive) corona discharge for 10 min. During biasing, the current density in the samples was 0.7 $\mu A/cm^2$. Under positive corona bias, electrons tunnel from the silicon substrate through the oxide into the nitride, where they can be trapped. We have utilized an etchback study and CV measurements to determine the charge centroid in our silicon nitride films after electron injection. Our results are consistent with others[5,6] who have previously reported that the charge distribution, though centered near the silicon dioxide–silicon nitride interface, extends well into the nitride bulk. After biasing, ESR measurements indicate a decrease in paramagnetic spin density of 1.1×10^{13} spins/cm^2 to a value of 2.5×10^{13} spins/cm^2, and CV measurements show that V_{mg} has shifted $+85$ V [Fig. 1(b)]. This shift corresponds to roughly 8×10^{12} trapped electrons/cm^2 in the silicon nitride, and this increase in the number of negatively charged centers is (within experimental error) equal to the decrease in the number of paramagnetic defects in the silicon nitride (Fig. 2). Electron trapping renders these formerly paramagnetic and neutral centers diamagnetic and negatively charged.
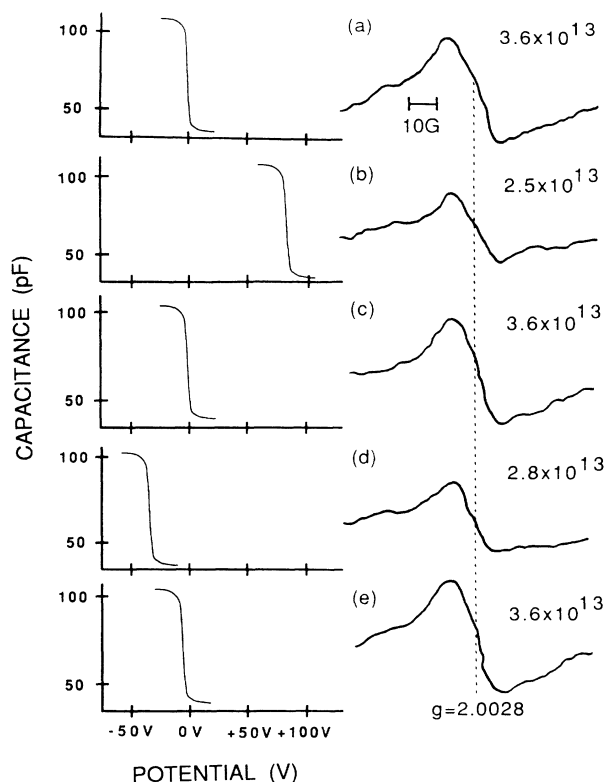

FIG. 1. ESR and CV data: (a) following 20 min of uv illumination; (b) following 10 min of positive corona biasing; (c) following a second 20-min exposure to uv illumination, the sample returns to its initial state; (d) following 10 min of negative corona biasing; (e) following a third 20-min exposure to uv illumination, the sample again returns to its initial state. The ESR traces are first derivatives (arb. units) of ESR absorption vs magnetic field. The spin density is indicated to the right of each resonance.
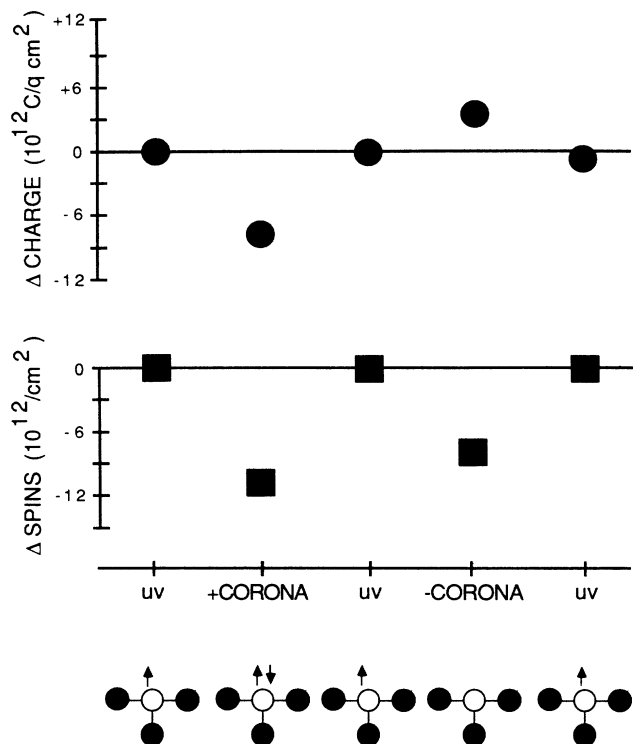
FIG. 2. CV (Δ charge) and ESR (Δ spins) data plotted to show the relative changes in paramagnetic and electrically active defect densities following biasing and illumination operations performed throughout the study. The charge and spin states of the defect at each point throughout the study are also shown. (q is the charge on an electron.)

Next, the samples were subjected to uv illumination for 20 min; the number of paramagnetic defects increased to 3.6×10^{13} spins/cm^2, and V_{mg} shifted -85 V back to the origin [Fig. 1(c)]. This could be explained several ways: one possible explanation is that the uv light photodepopulates the electrons previously trapped during biasing, which in turn eliminates any charge in the nitride. In any case, the space charge is annihilated by the uv illumination. The negatively charged centers' return to a paramagnetic state is accompanied by their loss of an electron. The silicon-dangling-bond center in amorphous silicon nitride is again neutral and paramagnetic. [The possibility of the large shift in the CV curve being caused by charge injection during the CV measurements has been ruled out; unstressed illuminated samples showed no charge injection when biased at voltages somewhat larger than those utilized in the CV measurements (± 100 V) for several minutes.]

The samples were at this point subjected to a negative bias (with respect to the Si substrate) using (negative)

corona ions for 10 min; current through the samples was the same as in the case of positive bias. Under negative corona bias, hole injection from the silicon takes place via tunneling, and holes are trapped in the nitride layer. Again, an etchback experiment was performed in conjunction with CV measurements to determine the charge centroid in our nitride films after hole injection. Again, we find that the centroid, although located near the silicon dioxide–silicon nitride interface, extends well into the nitride bulk. This biasing resulted in a decrease in paramagnetic center density of 8×10^{12} spins/cm^2 to a value of 2.8×10^{13} spins/cm^2. CV measurements indicate V_{mg} shifted -35 V, indicating roughly 3×10^{12} trapped holes/cm^2 [Fig. 1(d)]. The decrease in the density of paramagnetic centers is again (within experimental error) approximately equal to the number of charged centers in the nitride (Fig. 2). Holes trapped at the neutral paramagnetic centers render these centers positively charged and diamagnetic. Finally, the samples were illuminated with uv light for 20 min; the spin density increased by 8×10^{12} spins/cm^2 to its original value of 3.6×10^{13} centers/cm^2 and V_{mg} shifted $+30$ V to bring the midgap voltage to -5 V [Fig. 1(e)]. This is again consistent with the disappearance of holes at silicon-dangling-bond centers during uv illumination, rendering them paramagnetic and neutral.

In conclusion, we present for the first time, conclusive evidence that paramagnetic neutral silicon-dangling-bond defects in silicon nitride may capture either electrons or holes. The capture of either a hole or an electron renders the neutral defect diamagnetic and charged. These dangling bonds are on silicon atoms bonded to three nitrogen atoms. This defect is neutral in its paramagnetic state, and is roughly uniformly distributed through the bulk of the nitride films. When positively or negatively charged, these defects are diamagnetic; they can be returned to their neutral, paramagnetic state with the aid of 4.9-eV illumination. Our results suggest that this is the dominant defect responsible for the trapping observed in silicon nitride films used in nonvolatile memory devices and amorphous silicon thin-film transistors. Furthermore, our ability to cycle the defect between its paramagnetic neutral state and both its charged diamagnetic states suggests that the optical generation of dangling bonds in amorphous silicon nitride films involves no complex structural rearrangement, but simply changes in the charge and spin states of the defect.

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