Nitrogen Dangling Bonds in Hydrogenated Amorphous Silicon Nitride Thin Films

J. Kanicki, W.L. Warren* and E.H. Poindexter**

IBM Research Division, Thomas J. Watson Research Center Yorktown Heights, NY 10598
*Sandia National Laboratories, Albuquerque, NM 87185
**US Army ET&DL, Ft. Monmouth, NJ 07724

The photocreation mechanisms and properties of nitrogen dangling-bonds (N^{0} -centers) in amorphous hydrogenated N-rich silicon nitride thin films are investigated. We find that the creation kinetics depend on the post-deposition anneals; it is illumination temperature independent, and can be well described by a stretched exponential illumination time dependence function. The photocreated N^{0} -centers can be photobleached by sub-bandgap light. All these results suggest that the photocreation mechanism of the N^{0} -centers simply involves a change of spin and charge state of pre-existing diamagnetic nitrogen charged sites created by the post-deposition thermal treatment.

1. INTRODUCTION

The principle deep trap centers in amorphous hydrogenated silicon nitride (a-SiNx:H) thin films have been predicted to be silicon and nitrogen To date, the focus of most dangling-bonds.¹ electron paramagnetic resonance (EPR) studies in a-SiN_x:H thin films has been on the silicon dangling-bond (K⁰-center), primarily because other EPR-active centers evaded detection. Recently, another intrinsic defect center was discovered in amorphous silicon nitride and shown to be a nitrogen dangling-bond (N⁰-center).^{2 - 5} Because this defect could influence the electrical properties and/or stability of hydrogenated amorphous silicon (a-Si:H) and polycrystalline silicon (poly-Si) thin film transistors (TFTs) incorporating an amorphous silicon nitride gate dielectric, it is important to establish the relevance of this defect to TFT technol-This paper presents the experimental data ogy. focusing on the properties and microscopic origin dangling-bond nitrogen centers in the of hydrogenated N-rich amorphous silicon nitride films.

2. EXPERIMENTAL

The N-rich silicon nitrides having different thicknesses were deposited by PECVD on fused silica and c-Si substrates at substrate temperatures (T_s) of 250 and 400°C. The EPR measurements were made at X-band using a TE₁₀₄ cylindrical

cavity. A weak pitch standard was used to estimate the spin concentrations. Post-deposition annealing was performed in a small tube furnace at different temperatures for various times in dry nitrogen. Broad-band UV-illumination was done using an Oriel 100 W Hg arc lamp.

2. RESULTS AND DISCUSSION

Figs. 1 and 2 illustrate the EPR spectra for the undiluted and He-diluted N-rich silicon nitride films, respectively, subjected to identical treatment. The N^0 -center is identified by its 3-line EPR spectrum



Fig. 1. EPR spectra of an undiluted Nrich amorphous silicon nitride film subjected to different treatment indicated on the figure.





which re-sults from its nuclear spin I=1; the K⁰-center was identified by its zero-crossing g=2.0028. Although both films show similar trends in the evolution of the EPR spectra after identical treatment, there are two differences which should be noticed. First, the UV-illumination of asdeposited films generate both K⁰-centers and N⁰-centers in the He-diluted films; in contrast, only K⁰-centers are observed in undiluted films. Second, after identical anneal/UV sequence the density of



Fig. 3. Variation of the slope deduced from the inset of this figure as a function of the inverse of post-deposition and an inset the evolution of the nitrogen dangling-bonds comcentration with anneal time for different T_a is shown.

 N^0 -centers in the He-diluted films is always greater than that observed in the undiluted silicon nitrides films. This result indicates that in He-diluted films there is no need for the thermal anneal; only room temperature UV-illumination is needed to create a certain number of the N^0 -centers in these films.

To create the nitrogen dangling-bonds in undiluted N-rich nitrides a two step process is needed: anneal above Ts (step one) and subsequent UV-illumination (step two). Now we investigate the effects of thermal post-deposition anneal step while keeping the illumination time constant (1 hr for all annealing temperatures (Ta) and annealing times (t_a)). Fig. 3 summarizes our results. It will be shown below that the creation of the paramagnetic neutral centers from the diamagnetic charged nitrogen sites is not thermally activated. Therefore, as indicated in Fig. 3 the creation of charged nitrogen sites is only thermally activated. This thermal process of charged sites creation can be described by a simple exponential function which yields an activation energy (E_{ac}) of approximately 0.8 eV.

As mentioned earlier we now demonstrate that the N^0 -centers photocreation kinetics (step two) is independent of illumination (and measurement) temperature, i.e. it is not thermally activated, Fig. 4. The photocreation kinetics of N^0 -centers shown



Fig. 4. Creation kinetics of nitrogen dangling-bonds in N-rich silicon nitride at 300 and 100 K using broad-band UV-light. The illumination at a given temperature was done in-situ EPR cavity. The lines represent the theoretical fitting to a stretched exponential function given in the text.

in this figure can be fit by a stretched exponential function: N(t)=N(s)(1-exp(- $(t/\tau)^{\beta}$)); where N(t) and N(s) is the density of N⁰-centers at illumination time t and at saturation, respectively, τ is a time constant and β is a characteristic stretching parameter related to dispersive carrier transport. If the annihilation of excitons, diffusion of atomic hydrogen or bond-breaking events were involved in the creation of nitrogen dangling-bonds by UV-illumination, a temperature dependence would have been expected. This is not the case for the photocreation of N⁰-centers in N-rich silicon nitride films. Therefore, the creation of nitrogen danglingbonds in the N-rich films must be electronic in nature and it simply involves a change of spin and charge state of pre-existing diamagnetic positively (N⁺) and negatively (N⁻) charged nitrogen sites which are created during the post-deposition thermal anneal.

Finally, based on the IR spectra and hydrogen evolution with thermal annealing we think that the N-H group maybe a precursor to N⁰-center formation. The thermal evolution of hydrogen shown in Fig. 5 (for more details see ref. 7) clearly indicates that for post-deposition thermal anneals used in this study it is expected that the hydrogen will evolved from the film leaving behind the charged nitrogen sites. These charged nitrogen sites upon UV-illumination can trap electrons or holes and become paramagnetic N⁰-centers observed in N-rich films. Further support for this photocreation mech-



Fig. 5. Evolution of hydrogen as a function of temperature for undiluted and He-diluted N-rich silicon nitride films deposited at two different temperatures. This figure has been adopted from ref. 7.

anism is provided by the observation that the N⁰-centers can be photobleached⁶ by subbandgap light and the photobleaching phenomenon is reversible, i.e. the N⁰-centers can be reversibly and repeatedly photocreated and photobleached by different illumination conditions (5.2 eV and broadband UV-light, respectively). In addition, we have also found that the net space charge in the films does not change even though the nitrogen dangling-bonds concentration changes by $1 \times 10^{13} \text{cm}^{-2}$ aftermentioned in the photocreation/photobleaching sequences. Therefore, the paramagnetic nitrogen dangling-bonds most likely become compensated charged diamagnetic nitrogen sites through an optical rearrangement of charge, thereby explaining the decrease in the spin density without any change in the net space charge density.

3. CONCLUSION

The main conclusions of this investigation can be summed up in the following two points. First, we believe that the neutral state of nitrogen dangling-bonds is caused by simple optically induced rearrangement of charges in existing charged diamagnetic nitrogen centers in N-rich nitride films generated during the annealing process. Second, the N-H group is most likely a precursor to the nitrogen dangling bond formation; the evolution of hydrogen during or after the film deposition generates charged nitrogen sites that upon UV-illumination can trap charge carriers and become paramagnetic neutral centers. Based on our results we also conclude that in the as-deposited gate-quality N-rich films used in a-Si:H TFTs the nitrogen dangling-bond plays only a minor role in the gate dielectric instability. But this may not be the case for poly-Si TFTs.

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