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Processing Induced *Pre-Existing Vacated (Empty) O-atom* Defect Sites in Remote Plasma Deposited GeO_2 and SiO_2 Gate Dielectrics

Gerald Lucovsky[1], Jinwoo Kim[1], Kun Wu[1], Daniel Zeller[1], Brian Papas[2], Jerry L. Whitten[2]
[1]North Carolina State University, Department of Physics
2401 Stinson Drive, Raleigh, North Carolina 27695-8202, USA
Phone: +01-919-513-7116 E-mail: lucovsky@ncsu.edu
[2]North Carolina State University, Department of Chemistry

1. Introduction

SiO_2 is the standard by which alternative gate dielectrics are evaluated for potential device applications, including remote plasma deposited GeO_2 of this abstract [1]. There is interest in Ge as a channel material for scaled complementary MOS (CMOS) devices, particularly for p-MOSFETs with significantly larger channel mobilities than Si p-MOSFETs. Studies have generally employed Ge native dielectrics, GeO_2, GeON and Ge_3N_4, as interfacial layers and high-K dielectrics: HfO_2 and ZrO_2 [2]. P-MOSFETs fabricated on Ge in this way display performance acceptable for integration into nano-scaled CMOS, but this is not the case for n-MOSFETs [2]. This paper provides an explanation for this difference, and a solution for n-MOS devices on n-Ge substrates capped with 1 nm of c-Si.

2. Experimental Methods

Non-crystalline GeO_2 films were remote plasma deposited at 300°C onto Ge substrates after a final rinse in NH_4OH. Precursor gases are: (i) down-stream injected GeH_4 in He, and (ii) upstream, plasma excited O_2-He mixtures. Following 300°C deposition, GeO_2 films were annealed at 400°C to 700°C in Ar. Films annealed at 400°C displayed no evidence for loss of O and sub-oxide formation, and a 5-6 eV mid-gap absorption associated with GeO_x $x<2$ suboxide bonding. They are stable in laboratory ambients with no evidence for reaction with atmospheric water. Films deposited on Ge and annealed at 600°C and 700°C display spectra indicative of O-atom loss, with a characteristic 5.5 eV defect absorption, erroneously attributed to the band gap of GeO_2 [3]. X-ray absorption spectroscopy studies include comparisons with remote plasma-deposited SiO_2 on Si substrates. Three properties of remote plasma GeO_2 are addressed: differences between (i) conduction band and conduction band edge states of GeO_2 and SiO_2, (ii) electronic structure of process induced *vacated O-atom* pre-existing defects in GeO_2 and SiO_2, and (iii) differences in annealing of GeO_2 films on Ge substrates, Si substrates with SiON interfacial transition regions, c-Si capped Ge substrates.

3. X-ray Spectra/Data Reduction

Figure 1(left) compares O K edge spectra of ~5 nm thick films SiO_2 and GeO_2 remote plasma deposited at 300°C onto plasma nitrided surfaces of Si. The SiO_2 film was annealed in Ar at ~850°C, and no post-deposition annealing was done on the GeO_2 film. Energies of conduction band edge states, and pre-conduction edge electronic transitions and negative ion states have been obtained by X-ray absorption spectroscopy [5].

The "s-like" and "d-like" notations refer to atomic parentage of these Si 3s and 3d states. When renormalized to symmetry-adopted terms for tetrahedrally bonded Si, these transform respectively into (i) A_1 and B_1, and (b) T_2 and E term symmetries. Arrows indicate optical band-gaps of 8.9±0.1 eV for SiO_2 and 9.7±0.2 eV for GeO_2. These have been determined from a comparison between band edge features in 2nd derivative spectra in Fig. 1(right).

The band gap is defined at the excitation energy that is the threshold for photoconductivity. There are non-photo conducting excitonic states with a triplet character, and splitting induced by final state effects. The same band edge states for SiO_2 in Fig. 1(right) have also been detected in bulk-glasses of SiO_2.

Figure 2(left) indicates different O K edge spectra for 5 nm thick GeO_2 films deposited on a chemically clean Ge surface. One was annealed in Ar for ~1 minute at 400°C, and the second in Ar for ~1 minute at 700°C. The magnitude of the peak absorption in the 700°C annealed film is reduced with respect to that of the 400°C film, and all spectral features are broadened. Of particular importance is the broad sub-band-gap feature centered at about 530 eV. This feature is present in all films GeO_2 films deposited on Ge substrates annealed at 600°C and 700°C. It is due to a reaction between the GeO_2 and the Ge substrate with evolution of O. It is not detected in GeO_2 deposited on Si substrates and annealed at temperatures to 700°C [4]. These two observations are independent of surface preparation of the Ge or Si substrate prior to remote plasma deposition. All as-deposited GeO_2 films onto 300°C Ge substrates, and subsequently annealed in Ar at 400°C are essentially the same as the GeO_2 film in the 400°C plot in Fig. 2(left).

Fig. 2(right) is comparison of the O K pre-edge spectra for the same two annealing temperatures of 400°C and 700°C. The spectrum for the 400°C annealed film is the essentially the same for other 400°C GeO_2 films on Ge and Si substrates, and 600°C and 700°C films on Si substrates. This correlation between O K pre-edge and O K edge spectra applies to films that do not shown the marked change in the character of the O K edge spectra in the Ge film annealed to 700°C in Fig. 2(left). The films which display this change are deposited on Ge substrates, and the changes in the 700°C spectra deposited onto chemically cleaned Ge also occur for O_2/N_2 plasma processed Ge substrates.

Figure 3 displays an O K pre-edge high-resolution spectral trace for the SiO_2 film annealed at 950°C. Features in this plot include (i) the band-gap for photoconductivity at 530.5

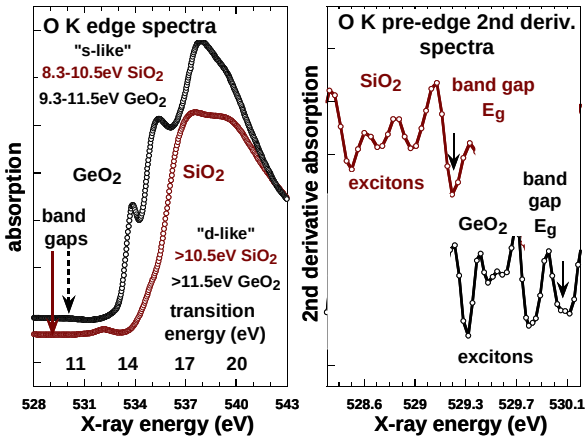

Fig. 1. Remote plasma GeO_2 and SiO_2 films: (left) O K edge, (right) pre-edge 2nd derivative band edge features.

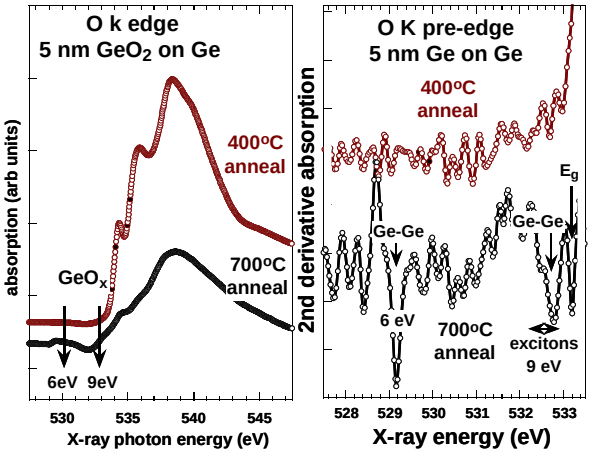

Fig. 2. Remote plasma GeO_2 films annealed at 400°C and 700°C: (left) O K edge, (right) pre-edge 2nd deriv.

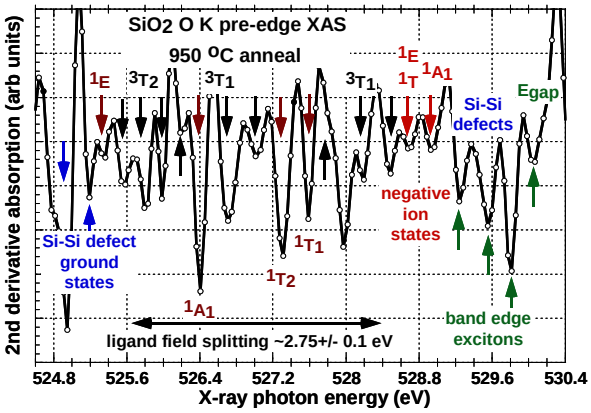

Fig. 2. Remote plasma SiO_2 films annealed at 950°C. O K band edge features and pre-edge pre-existing defects associated with vacated O atom sites. Si-Si defect ground features are not detected in films processed at 850°C.

eV, (ii) band edge excitons at 529.8 eV, 529.6 eV and 528.4 eV, (iii) three negative ion singlet states between 528.4 and 529.0 eV, (iv) three groups of triplets, nine states, and three singlet states embedded in a common spectral regime, (v) a singlet E_g state, and finally (vi) singlet and triplet ground states. Labeling of these states is from Tanabe-Sugano (T-S) diagrams for tetrahedrally-bonded Si, and is valid for intermediate values of the ligand field splitting, Δ_{LF}. For SiO_2, Δ_{LF} = 2.75±0.15 eV, and is obtained from the spectral width of triplet features in Fig. 3. This fit to the SiO_2 pre-edge O K spectra demonstrates that the interpretation of the GeO_2 spectra in Fig. 2. (right) is a valid approach for identification of features in plasma GeO_2 O K pre-edge 2nd derivative spectra. A previous assignment for pre-existing defects in SiO_2 thin films processed at different fictive temperatures, and assigned to small regular rings including three and four Si atoms, [6] respectively is not supported either by theory or the results in Fig. 3.

4. Summary

(i) Spectral features in remote plasma CVD GeO_2 films deposited on Ge and Si substrates and annealed, respectively, to 400°C and 700°C, are sharper than features in plasma deposited SiO_2 annealed to ~900°C. (ii) The band-gap, and band edge excitons in GeO_2 are shifted to higher energies by ~0.8 eV in GeO_2 compared with SiO_2. (iii) Sub-band-gap defects, detected by 2nd derivative XAS in the O K pre-edge regime, are due to vacated (or empty) O-atom sites. (iv) Temperature dependent increases in pre-existing E' ESR defects are explained quantitatively by quantum chemistry calculations and empirical reaction kinetics. (v) In contrast, ESR studies in X-ray and γ-ray irradiated SiO_2 include *additional non-bridging oxygen hole centers* that are associated with the O-atoms originally in Si-O-Si sites that are activated by more efficiently by γ-ray *irradiation* [8]. (vi) The increased band gap of GeO_2 with respect to SiO_2, and suppression of GeO_x formation on Si for 700°C anneals are the basis for nm scaled GeO_2-nm Si-capped Ge n-MOS devices. (vii) EOT's of ~0.8 nm were obtained for $(HfO_2)_{0.3}(SiO_2)_{0.3}(Si_3N_4)_{0.4}$, films 2 nm thick on n-MOS Ge devices capped with ~1 nm of c-Si [7]. Interfacial defects are in the 10^{11} cm^{-2} range for GeO_2 as well, 10 times lower *with respect to those reported in* Ref. 2.

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