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DEGRADATION OF RELIABILITY OF HIGH-K GATE DIELECTRICS CAUSED BY POINT DEFECTS AND RESIDUAL STRESS

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PURPOSE

In this study, the degradation mechanism of dielectric properties of hafnium dioxide thin films was investigated by using quantum chemical molecular dynamics. Effects of point defects such as oxygen vacancies and carbon interstitials and residual stress in the films on their local band gap were analyzed quantitatively. Drastic decrease of the local band gap from about 5.7 eV to about 1.0 eV was caused by the formation of a defect-induced site in the band gap. Though this defect-induced site was recovered by additional oxidation, the remaining interstitial oxygen deteriorated the quality of the interface with tungsten electrode by forming new oxide between them. The estimated changes of the band gap and the interface structure were confirmed by experiments using synchrotron-radiation photoemission spectroscopy. [Keywords: High-k Gate Dielectrics, Band Gap, Point Defects, Residual Stress, Hafnium Oxide, Quantum Chemical Molecular Dynamics, Synchrotron-radiation Photoemission Spectroscopy]

ANALYTICAL MODEL AND RESULTS

The point defects in gate oxide thin films in the miniaturized transistors play an important role in the degradation of the transistor performance because the relative volume ratio of weak spots caused by point defects has become larger and larger. The residual stress in the film caused by the intrinsic stress in the gate electrode and interconnection films has been also increasing due to strained silicon technology. [1] Such point defects and stress often deteriorate the electronic quality of the gate oxide film. For example, it was found that oxygen vacancies generate donor sites in the band gap of the film and tensile stress in the film decreases its band gap. [2][3]

To make clear the formation mechanism of the point defect-induced impurity states in the gate oxide film, quantum chemical molecular dynamics was applied. In this analysis, an extend Hückel approximation was used to solve the electronic state. The empirical parameters used in Hamiltonian were optimized on the basis of density functional theory (DFT) calculations and the experimental results. In this study, the structural and electronic properties of monoclinic HfO_2 with oxygen vacancies and carbon interstitials were analyzed by using a three-dimensional atomic model as shown in Fig. 1. The band gap of HfO_2 was defined as the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The local band gap of the film around an oxygen vacancy was found to decrease drastically from about 5.7 eV to about 1 eV as shown in Fig. 2. This is because that an extra "HOMO" peak appears in the band gap due to the oxygen vacancy. This defect-induced site is formed by the dangling 5d orbital of a hafnium atom. Carbon interstitials that is often introduced by atomic layer deposition (ALD) or metal-organic chemical vapor deposition (MOCVD) process using an organic source also decrease the effective band gap of the film. The interstitial carbon atoms interact with hafnium atoms, i.e., deoxidize the hafnium oxide, and thus, easily make oxygen vacancies. Sometimes the carbon interstitials substitute into the vacant oxygen sites and form Hf-C bonds. Such formation of oxygen vacancies generates the donor states in the band gap of hafnium dioxide. When additional interstitial oxygen atoms exist near the vacant sites, they easily occupy the sites, and thus recover the defected sites. Therefore, oxidation after the film deposition using ALD or MOCVD using an organic source is effective for improving the film quality. Figure 2 summarizes the point defect-induced impurity states in the hafnium

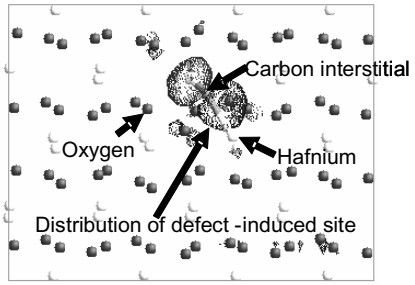

FIGURE 1. CARBON INTERSTITIAL-INDUCED DEFECT SITE IN HAFNIUM DIOXIDE

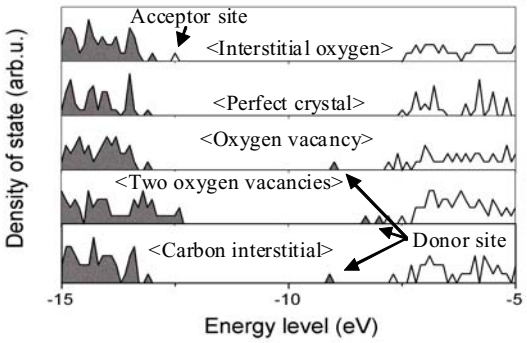

FIGURE 2. POINT DEFECTS-INDUCED IMPURITY STATES IN THE BAND GAP OF HAFNIUM OXIDE.

dioxide. Excessive interstitial oxygen atoms generate acceptor states in the band gap. Other defects; oxygen vacancies, carbon interstitials generate donor states in the band gap. Therefore, composition control of hafnium dioxide is very important to assure the electronic quality of the film.

PHOTOEMISSION SPECTROSCOPY AND RESULTS

The estimated point defects-induced change of the bad gap of $HfO_{2-x}C_y$ films was validated by synchrotron-radiation photoemission spectroscopy. A high-energy excitation source (5947.9 eV) enabled the analysis of the chemical shift of the component elements in the 4-nm thick $HfO_{2-x}C_y$ films with metal gate of 4-nm thick tungsten. Two kinds of 4-nm thick hafnium dioxide thin films were deposited by ALD. One film contained a large density of carbon interstitials and oxygen vacancies. Another one held a lower density of them. The relative peak intensities of O-1s, Si-2p, and Hf-4f, for example, were compared with each other to evaluate the defect density in the films.

The binding energy of Hf-4f clearly shifted to the higher binding energy side when the defect density was low, in Fig. 3. This chemical shift indicates that the atomic bonding condition became unstable when the defect density was high. In addition, the change of the peak position of the sub peak that appeared at the binding energy higher than 23 eV indicates the change of the band gap structure of the films. The width of the peaks of the film with low density of the defects was wider than that with high density of the defects. This increase of the peak width may indicate the increase of residual strain in the film. Similar shift and change were observed in O-1s peak of both films.

The reduction of oxygen vacancies and carbon interstitials in the $HfO_{2-x}C_y$ films increased the band gap of the films significantly as shown in Fig. 4. The change of the band width was about 1 eV. This result clearly shows that the increase of point defects such as oxygen vacancies and carbon interstitials decreases the band gap of hafnium dioxide films and deteriorates the film quality.

The deposition of a tungsten gate electrode on the hafnium oxide film also affects the film quality as shown in Fig. 5. The binding energy of Hf-4f shifted to the lower energy side and a new strong peak of O-2s appeared at about 23 eV. Similar change was observed in the spectra of W-4d and W-4f. These changes of chemical bonding conditions in the hafnium oxide and tungsten films indicated the deoxidization of the $HfO_{2-x}C_y$ film and the formation of tungsten-oxide due to the excessive oxygen interstitials that were introduced into the film by post-oxidation after the ALD. The composition control of the $HfO_{2-x}C_y$ film before deposition of the tungsten electrode film, therefore, should be optimized for improving the quality of the gate-stack structure of hafnium dioxide.

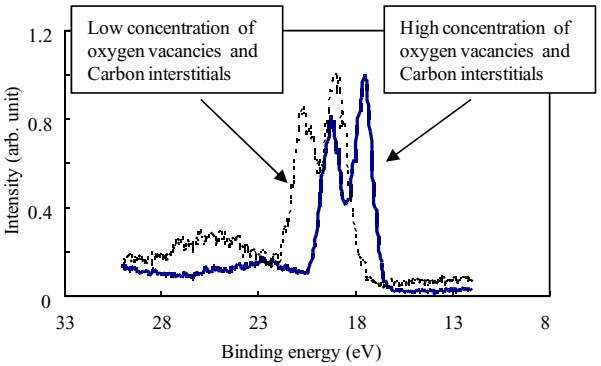

FIGURE 3. POINT DEFECTS-INDUCED IMPURITY STATES IN THE BAND GAP OF HAFNIUM OXIDE.

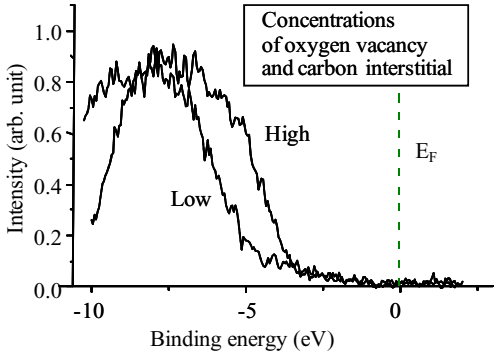

FIGURE 4. SYNCHROTRON-RADIATION PHOTOEMISSION SPECTRA OF THE $HfO_{2-x}C_Y$ FILMS NEAR THE EDGE OF THE FERMI LEVEL.

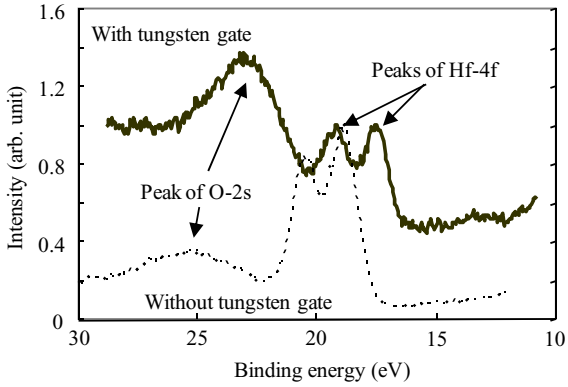

FIGURE 5. CHANGE OF BINDING ENERGY OF HAFNIUM 4-F DUE TO DEPOSITION OF A TUNGSTEN GATE ELECTRODE FILM.

CONCLUSION

Point defects such as oxygen vacancies and carbon interstitials deteriorate the electronic quality of hafnium dioxide thin films by formation of the dangling 5d orbital of a hafnium atom. The degradation can be recovered by additional oxidation of the film. The gate electrode formation on the film also degrades the film quality. Therefore, the minimization of both point defects and residual stress in the hafnium dioxide film is indispensable for improving the electronic performance and reliability of the film.

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