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Direct evidence of localized states in high-k materials for gate insulator - Cathode luminescence study of HfO_2 films -

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Abstract

Information on localized states in HfO_2 has been obtained as a function of annealing temperature by means of cathode luminescence (CL). CL spectra showed two peaks of 4.3 eV and 3.4 eV. The 4.3 eV peak is suggested to originate from band-tail electron-hole recombination, while the 3.4 eV peak is tentatively assigned as defect luminescence. It is shown that non-radiative recombination path through defect states monotonously decreases with an increase in annealing temperature.

1. Introduction

High-k materials for gate insulators need not only high susceptibility and thermal stability but also low leakage current and good interface properties. Insulators generally contain localized-states in the band gap which can be an origin of the leakage current. At the present stage, however, there is no direct measurement technique to detect the localized states in high-k materials, although electrical measurements can offer some insights in the localized states. Luminescence is a standard technique to detect localized-states in semiconductors and insulators, while for wide band-gap materials it is not so easy to use ultra-violet light as an excitation source. Here, to study the localized states in high-k materials we have utilized an electron beam for excitation of electron-hole pairs instead of ultraviolet light, namely cathode luminescence (CL) [1]. In this report, we present the results of CL in HfO_2 as a standard high-k material.

2. Experimental

HfO_2 films were deposited on a Si (100) substrate using a KrF pulsed laser deposition technique at 200 ℃ in 100 mTorr nitrogen atmosphere. The film thickness was around 100 nm. Thermal annealing was performed in 1 atm oxygen gas for 10 min with a 100°C step from 300°C to 800°C.

Luminescence excited by 10 keV electron beam irradiation with several 10 nA at room temperature was detected by CCD through an optical fiber. Electron excitation depth that is a function of acceleration voltage is around 10 nm for 10 keV. Therefore, all luminescence light is considered to come from HfO_2 films. To evaluate how deep the band tail states expand into the band gap we have used photoacoustic spectroscopy (PAS). PAS technique directly detects heat generated by light absorption using a microphone located close to a sample. Roughly speaking the PAS intensity is proportional to optical absorption coefficient in the low optical absorption range of 10-10^3 cm^{-1} for a 1-μm sample [2]. PAS measurements have been performed using 1-μm thick HfO_2 films deposited on fused silica substrates.

3. Results and Discussion

Annealing technique is important to modify or improve material properties and an inevitable process for device fabrications. To detect the change of localized states in HfO_2 we have performed CL as a function of annealing temperature from 300°C to 800°C. CL spectra of an as-deposited sample and of samples with T_a = 400°C, 600°C, and 800°C are plotted in Fig. 1. CL spectra changed drastically depending on T_a. This shows that the localized states in HfO_2films sensitively changes with T_a, because the luminescence spectra are generally sensitive to localized states in the gap. This is the first observation indicating a change of the localized states in high-k materials with annealing. Since the leakage current also depends on the annealing temperature, it is likely that a change of leakage current is caused mainly by a change of localized states distribution.

As seen in Fig. 1, CL spectra have two peaks at 4.3 eV (290 nm) and 3.4 eV (370 nm). The peak intensities are plotted as a function of T_a in Fig. 2. The 4.3 eV peak monotonously increases with annealing temperatures, while the 3.4 eV peak has a maximum intensity around 400 °C.

Excited electrons and holes recombine through radiative and non-radiative processes as schematically shown in Fig. 3. Radiative processes are generally due to band edge recombination, band tail recombination, or recombination through defects. On the other hand, there are non-radiative recombination processes through defect states.

Orera et al. [3] showed that for yttrium stabilized crystalline ZrO_2 the optical absorption tail expands roughly to 3.9eV (320nm). Since the band gap of ZrO_2 is close to that of HfO_2 around 6.0 eV [4] and both materials have similar physical and chemical properties, it is reasonable to interpret that HfO_2 also has the band tail states extending down to around 4 eV. Therefore, the 4.3 eV peak obtained in this CL study is thought to originate from the band tail luminescence. To examine the optical absorption spectrum of HfO_2 used here we have performed PAS measurements, although exact conversion from a PAS signal to absorption coefficient is not made at the present stage. Figure 4 shows the PAS spectrum of an as-deposited 1-μm thick HfO_2 film. To get rough estimation of absorption coefficient, we have compared Fig. 3 with other material data like hydrogenated amorphous silicon [2]. A range of the PAS spectrum of Fig. 3 roughly corresponds to the absorption coefficient range from 10^1 to 10^3 cm^{-1}. We have clearly detected a PAS signal around 400 nm (3.1 eV), which means that for a HfO_2 film the band edge

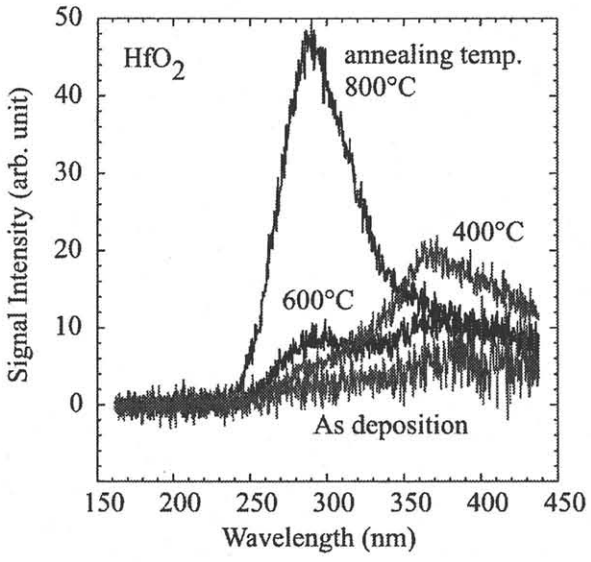

Fig. 1 Cathode luminescence spectra of HfO_2 films for as deposited sample (Ts = 200°C) and T_a = 400°C, 600°C, and 800°C samples.

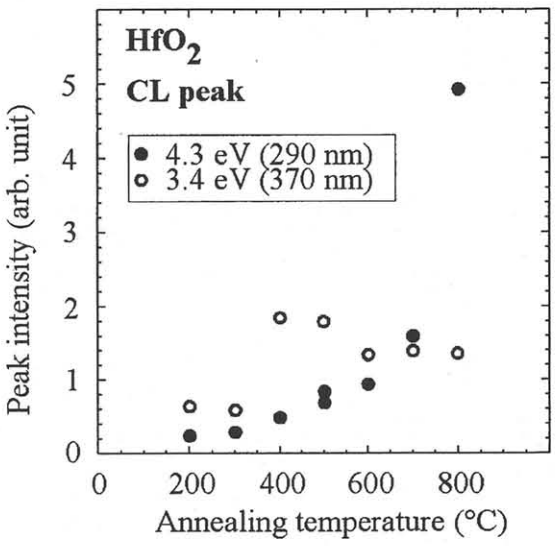

Fig. 2 CL peak intensity of two peaks at 4.3 V and 3.9 eV as a function of annealing temperature.

states expand into mid-gap due to amorphous and/or ionic material nature. This is consistent with the above speculation that the high-energy CL peak of 4.3 eV arises from the band tail emission.

The experimental result that the CL peak of 4.3 eV increases with annealing temperature suggests that the defect states contributing to non-radiative recombination decreases with an increase in annealing temperatures. Regarding the 3.4 eV emission peak, it depends on the preparation conditions, such as atmosphere (O_2 or N_2) during PLD deposition, suggesting defect related luminescence. Also luminescence from d-electron states cannot be ruled out.

4. Conclusions

We have first obtained the information about the localized states in HfO_2 films as a function of annealing temperature. The results showed that the defect states contributing to a non-radiative recombination process decreases with an increase of T_a. The high potential of CL to characterize high-k materials has been demonstrated.

Acknowledgments

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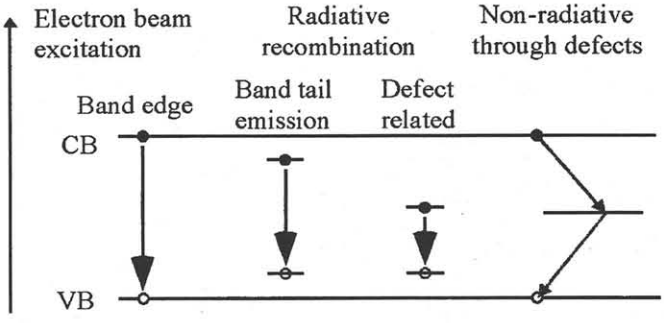

Fig. 3 Paths of electron-hole recombination.

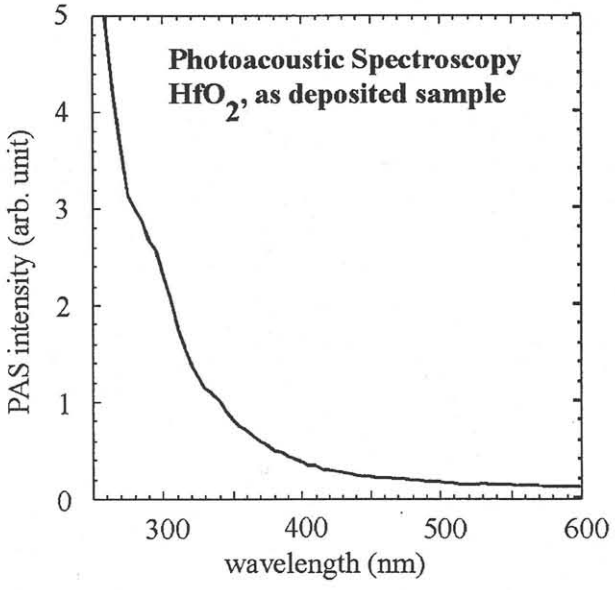

Fig. 4 Photoacoustic spectrum (PAS) of as-deposited HfO_2 film. The sample was deposited on a fused silica substrate.