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ESR and PL Study of Charge Trapping Centers in Silicon Nitride Films and Its Verification with Novel ONO-Sidewall 2-bit/cell Nonvolatile Memory

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1. Introduction

Defect centers in silicon-nitride (SiN) films are applied to charge-trapping nonvolatile memory devices [1]. In order to realize high density cell and high speed programming, it is required to investigate the defect structure in detail. Here, we have studied the defect state in LPCVD-SiN films fabricated of various ratios of SiH₄/NH₃ mixture gasses, by using electron spin resonance (ESR) and photoluminescence (PL) techniques [2]. We have discussed a relation between defect density and energy levels in the band gap of SiN films. Moreover, we have verified the nonvolatile memory characteristics of the SiN films by applying to novel oxide/nitride/oxide (O/N/O) sidewall 2-bit/cell nonvolatile memory, which provides not only excellent scalability 3F²/bit for high density storage application but also a low cost for embedded application. A 70nm device shows high performance 2-bit/cell operation.

2. Experimental

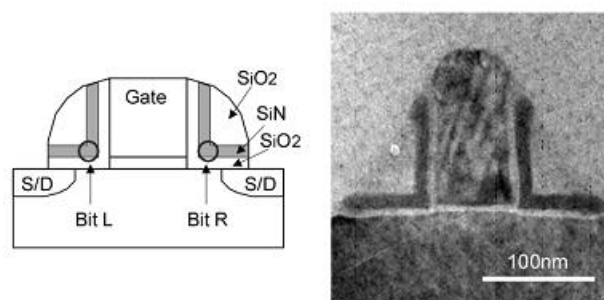
Evaluation samples are 100nm-thick LPCVD-SiN films fabricated on 10 ohm-cm (100) Si substrates at 800°C using SiH₄/NH₃ mixture gasses of A (1:5000), B (1:2000), C (1:100), and D (1:12.5).

The ESR measurements were done at room temperature on an X-band spectrometer (RE-1X). The external magnetic field (H) was modulated by 0.2 mT. The microwave power was 1mW. To actualize the paramagnetic defects (K center) in the SiN film, the samples were illuminated for 120 min with 254nm-UV light. We introduced the effective g-value ($g_{\text{eff}} = hv/\mu H$) as a lateral axis to compare the ESR spectra of different samples.

The PL measurements were also done at room temperature on a fluorophotometer (RF-5300PC). We translated the value of PL emission wavelength (λ) to the energy ($E = hc/\lambda$), in order to know the emission energy levels in the band gap of SiN films, where the photo-excited electrons are thought to stay temporally and recombine with the holes at valence band.

We have developed ultimately simple and scalable 2-bit/cell nonvolatile memory transistor. The memory cell consists of a conventional MOSFET without LDD. Figure 1 (a) and (b) are the schematic view of the proposed memory and TEM image of 70nm-node memory device, respectively. The L-shaped ONO films are formed on both sides of the gate electrode, constituting the sidewall spacers

which act independently as a storage (Bit L and Bit R). This memory device has a remarkable feature that the fabrication process is highly compatible with conventional CMOS logic process. We measured the nonvolatile memory characteristics of the SiN films fabricated under the conditions of the SiH₄/NH₃ mixture gasses. As is shown in Fig. 2, the silicon (Si) and nitrogen (N) network varied from N-rich to Si-rich in the SiN films according to the ratio of the SiH₄/NH₃ mixture gasses.



(a) the schematic view of the memory transistor. (b) cross-sectional TEM image of 70nm-node memory device.
Fig.1 The proposed ONO-sidewall 2-bit/cell nonvolatile memory.

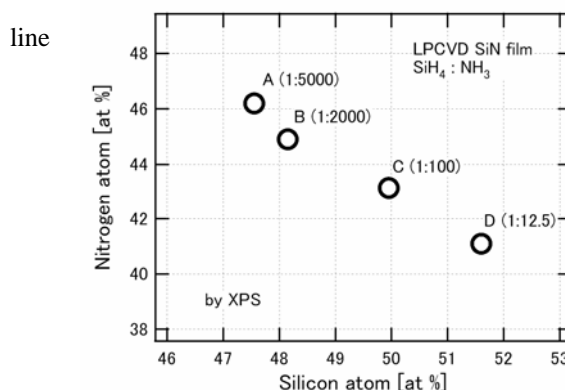


Fig. 2 The contents of Si and N atoms in the LPCVD SiN films.

3. Results and discussion

Figure 3 shows ESR spectra from the LPCVD-SiN films fabricated using SiH₄/NH₃ mixture gasses. K center due to Si dangling bond was observed clearly in case of sample C (1:100) and D (1:12.5) after UV illumination.

P_{b0} center was also observed at the interface of the SiN film and Si substrate. The K-center defect spin densities of Si-rich C and D samples were derived to be 2.9×10^{18} and $3.5 \times 10^{18} \text{ cm}^{-3}$, respectively.

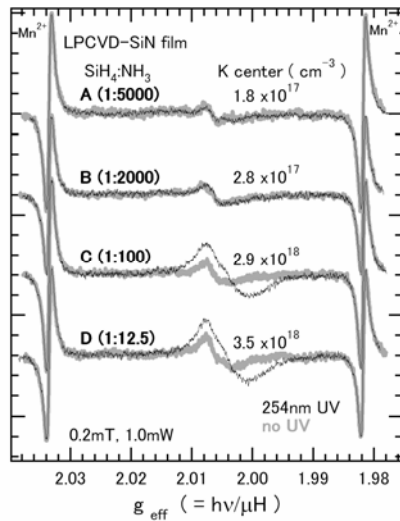


Fig. 3 The ESR spectra from the LPCVD-SiN films.

PL emission spectra have been obtained from the LPCVD-SiN films fabricated using SiH_4/NH_3 mixture gases. The four PL emission energy levels (E_a 4.78, E_b 4.42, E_c 3.98, and E_d 3.80eV from valence band level of SiN film) were derived from the sample C. Each emission peak had a half width of about 0.2eV. Moreover, two levels (E_e 3.30 and E_f 2.30eV) were derived from the spectra of sample A, B, C and D, as is shown in Fig. 4. PL emission energy levels of E_c and E_d shifted to lower direction with varying SiH_4/NH_3 mixture gas ratios from 1:5000 to 1:12.5. From the results of ESR and PL evaluation, we have found a relation that the PL-emission levels of E_c and E_d shift to lower level with the increase of K-center (charge-trap) density.

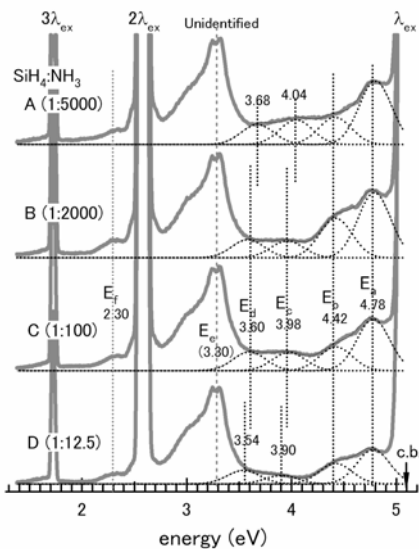


Fig. 4 PL emission spectra from the LPCVD-SiN films.

We have applied the various LPCVD-SiN films fabricated with different SiH_4/NH_3 mixture gas ratios to 70nm-node O/N/O sidewall 2-bit/cell nonvolatile memory. As a result, we have optimized the SiH_4/NH_3 mixture gas ratios and obtained the performance of nonvolatile memory characteristics, as are shown in Figs 5 and 6.

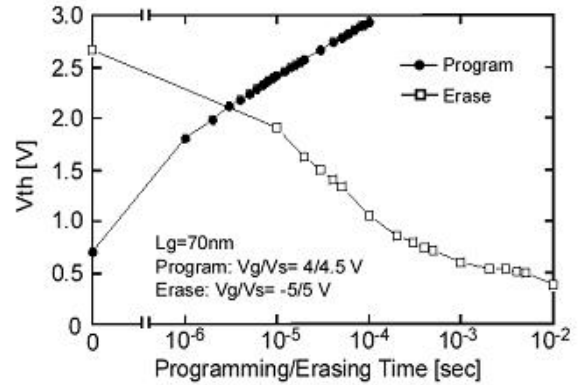


Fig. 5 Programming speed of 70nm-node O/N/O sidewall 2-bit/cell nonvolatile memory.

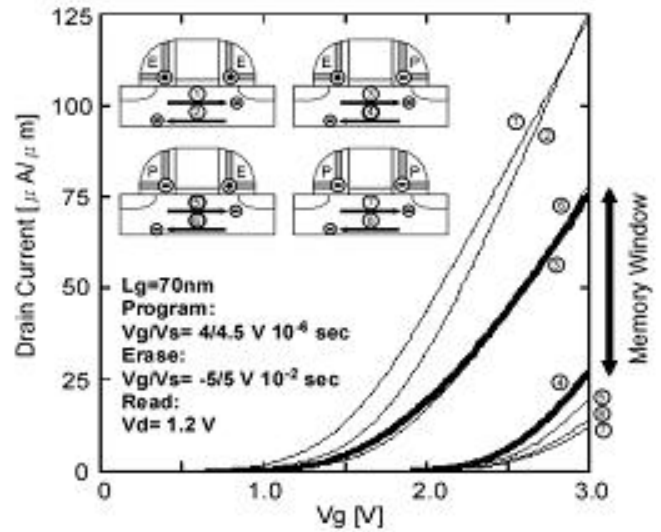


Fig. 6 Memory window of 70nm-node 2-bit/cell memory.

3. Conclusions

In the LPCVD-SiN films, with increase of SiH_4/NH_3 mixture gas ratio, we have found the paramagnetic defect density becomes larger and some PL emission energy levels become lower. This energy level lowering is thought to be caused by the overlapping of charge-trap potentials. We also verified the charge-trapping nonvolatile-memory characteristics by applying the LPCVD-SiN films to the 70nm-node ONO-sidewall 2-bit/cell nonvolatile memories.

References

- [1] Y. Kamigaki, S. Minami; IEICE Trans. Electron. **E84-C** (2001) 713-723.
- [2] Y. Shishido et al.; 207th ECS mtg. (Quebec City, 2005).