Influence of high-temperature thermal annealing on paramagnetic point defects in silicon-rich silicon nitride films formed in a single-wafer-type low-pressure chemical vapor deposition reactor

Kiyoteru Kobayashi; Ryo Miyauchi; Kenshi Kimoto

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Influence of high-temperature thermal annealing on paramagnetic point defects in silicon-rich silicon nitride films formed in a single-wafer-type low-pressure chemical vapor deposition reactor

Kiyoteru Kobayashi,1,a) Ryo Miyauchi,2 and Kenshi Kimoto1

AFFILIATIONS
1ESCO, Ltd., Oak Bldg 3F, 1-3-12 Nishikubo, Musashino, Tokyo 180-0013, Japan
2Graduate School of Engineering, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan

a)Author to whom correspondence should be addressed: kobayashi@escoltd.co.jp

ABSTRACT
The influence of high-temperature thermal annealing on silicon dangling bonds called K centers in Si-rich silicon nitride films grown in a single-wafer-type low-pressure chemical vapor deposition reactor with the SiH2Cl2-NH3 system at 750 °C has been investigated by combining thermal desorption spectroscopy (TDS), Fourier transform infrared spectroscopy-attenuated total reflection, spectroscopic ellipsometry, and electron spin resonance. In the TDS analysis, H2 desorption from the nitride films was detected above about 600 °C. It is found that thermal annealing at 750 and 900 °C caused a slight decrease in the K center density and a change in the g value of K centers, which are considered to be caused by changes in the atomic structure of the nitride films. On the other hand, thermal annealing at 1050 °C resulted in a substantial decrease in the K center density and the generation of paramagnetic defects with unprecedented characteristics. The findings in this study are expected to provide important guidelines for the design of manufacturing processes of nonvolatile memories.

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I. INTRODUCTION
Amorphous silicon nitride (a-SiNx) has attracted considerable attention as a key dielectric material to fabricate NAND-type flash memory1–6 and embedded nonvolatile memory.7 Several kinds of point defects existing in silicon nitride films, such as Si dangling bonds, Si–Si bonds, and H-related defects, generate localized energy states in the forbidden band, which affect the electrical properties of the nitride films.8–36 Therefore, extensive studies have been conducted to understand the nature of the point defects.

The previous studies using electron spin resonance (ESR) showed that paramagnetic point defects were generated by exposing silicon nitride films to high-energy ultraviolet (UV) light, which are called K0 centers.21,23,24 Valentin et al. revealed using density functional theory calculations that an isolated silicon dangling bond with an unpaired electron is the K0 center.32 The research results regarding isolated silicon dangling bonds are summarized as follows:

(i) there are three charge states in isolated silicon dangling bonds;
(ii) positively charged K+ and negatively charged K− states, which have no unpaired electrons and ESR-inactive, are converted into neutral charged ESR-active K0 centers by the UV exposure of silicon nitride films;9,23,29,30 (iii) K0 centers act as generation centers of electron-hole pairs when silicon nitride films are in a high electric field;33,34 (iv) thermal annealing at temperatures lower than 400 °C returned some K0 centers into K+ and K− centers and the subsequent UV exposure reproduced K0 centers;37 (v) the transformation between ESR-inactive K+ and K− states and ESR-active K0 state is repeatable by UV exposure and low-temperature annealing (≤400 °C).23,37

However, the thermal stability of K centers at high temperatures is still unclear. In the present work, we have studied the influence of high-temperature annealing on K centers in silicon nitride films formed using a low-pressure chemical vapor deposition (LPCVD) technique by combining thermal desorption spectroscopy (TDS), Fourier transform infrared spectroscopy-attenuated total reflection...
(FTIR-ATR), spectroscopic ellipsometry, and ESR. In addition, we have reported that isothermal annealing at 1050 °C resulted in the formation of paramagnetic point defects with unprecedented characteristics in the nitride films.

II. EXPERIMENT

After RCA cleaning and a short immersion in the aqueous hydrofluoric acid (HF) of p-type (100) silicon substrates, amorphous silicon nitride films with thicknesses ranging from 205 to 224 nm were deposited with SiH2Cl2 and NH3 gases at 750 °C using a single-wafer-type LPCVD reactor on the silicon substrates. The composition ratio x of nitrogen to silicon of the nitride films was found to be 1.31 by combining high-resolution Rutherford backscattering spectroscopy and x-ray photoelectron spectroscopy. TDS measurements were conducted under an ultrahigh vacuum condition at a linear heating rate of 60 °C/min using an ESCO infrared-heating-type thermal desorption analyzer TDS1200II.

Next, some of the fabricated samples were isothermally annealed at 400, 750, 900, and 1050 °C in a nitrogen ambient at atmospheric pressure. The thickness t0 and refractive index of the nitride films were measured using a SOPRA MOSS-ESVG spectroscopic ellipsometer. FTIR-ATR spectroscopy was carried out using a JASCO FT/IR-4600 spectrometer. ESR spectroscopy was performed using a JEOL JFS-FA200 X-band spectrometer at room temperature. The external magnetic field was modulated with an amplitude of 0.3 mT at a frequency of 100 kHz. The paramagnetic defect density was estimated by comparing the double numerical integral of the measured derivative power absorption spectrum with that obtained from a calibrated standard.

After isothermal annealing at 400, 750, 900, and 1050 °C, the nitride films were exposed to UV illumination at room temperature in a nitrogen atmosphere using the monochromatic light of a wavelength of 254 nm (4.9 eV). UV exposure and ESR measurements were alternatively conducted.

III. RESULTS AND DISCUSSION

TDS spectra usually consist of several desorption peaks, each of which is associated with a different thermal activation process. Figure 1 shows the TDS spectrum of the H2 desorption rate measured for the 209 nm-thick nitride film. H2 molecules were detected above about 600 °C. Two different peaks of the H2 desorption rate were clearly observed at 880 and 1180 °C. The number of desorbed N2 molecules was negligible in the range from room temperature to 1270 °C.

Next, the effects of thermal annealing at 900 and 1050 °C on the thermal stability of chemical bonds, the thickness and refractive index of the nitride films were investigated. These temperatures correspond to the temperatures within the two peaks at 880 and 1180 °C in the H2 desorption rate, respectively. The areal densities of N–H and Si–H bonds in the nitride films subjected to isothermal annealing at 900 and 1050 °C are shown in Fig. 2(a) as a function of annealing time, which were estimated from the FTIR-ATR spectra of the N–H stretching mode at 3350 cm−1 and the Si–H stretching mode at 2180 cm−1 using the empirical equation.26 The densities of N–H and Si–H bonds decreased rapidly with increasing annealing time. It is obvious that H atoms dissociated from N–H and Si–H bonds during thermal annealing at 900 and 1050 °C. The sum of the N–H and Si–H bond densities decreased by annealing at 1050 °C for 500 min was (9 ± 3) × 1016 cm−2, which was close to the density of H atoms desorbed in the temperature range from 600 to 1050 °C in the TDS measurement [(9.8 ± 0.6) × 1016 cm−2], despite the differences in the processing pressure and temperature profile. It is suggested that the desorption of H2 molecules shown in Fig. 1 is mainly due to the dissociation of H atoms from N–H and Si–H bonds.

Figures 2(b) and 2(c) show the film thickness and the refractive index at a wavelength of 632.8 nm as a function of annealing time. The nitride films shrank by 8% and 12%, respectively, and the refractive indices became higher owing to 900 and 1050 °C annealing for 500 min. It is claimed that the shrinkage of the nitride films caused the densification of the films, which was responsible for the change in the refractive indices.

ESR spectra of the 224 nm-thick nitride film subjected to the UV irradiation of 0, 0.02, and 1.04 kJ/cm2 before thermal annealing are shown in Figs. 3(a)–3(c). The small signal of the interface states, which are called Pso centers, was observed at a g value of 2.0060 before UV exposure, as shown in Fig. 3(a). The signal intensity increased and was saturated with increasing UV radiation dose from 0 to 1.04 kJ/cm2, as shown in Figs. 3(b) and 3(c). The ESR signals generated by UV exposure were characterized by a g value of 2.0031 ± 0.0001 and peak-to-peak linewidth 2ΔHpp of 1.24 ± 0.03 mT. The paramagnetic defect density was estimated to be 2.2 ± 0.5 × 1019 cm−2 from the saturated ESR signal. Subsequently, the UV-irradiated nitride films were isothermally annealed at 400, 750, 900, and 1050 °C.

Figures 3(d) and 3(e) show the ESR spectra obtained from the nitride film annealed at 900 °C for 50 and 500 min, respectively. The signal induced by UV irradiation once disappeared owing to
annealing at 900 °C for 50 min. After the nitride film was annealed at 900 °C for 500 min, there was no noticeable change in the spectrum, as shown in Fig. 3(e). The subsequent UV exposure again generated paramagnetic defects, as shown in Fig. 3(f). The paramagnetic defect density was estimated to be $1.7 \times 10^{14}$ cm$^{-2}$ from the saturated ESR signal after long-term UV irradiation. In addition, the $g$ value and $\Delta H_{pp}$ were obtained to be $2.0024 \pm 0.0002$ and $1.43 \pm 0.05$ mT, respectively.

Figures 4(a) and 4(b) show the paramagnetic defect density and $g$ value obtained from the saturated ESR signals after long-term UV irradiation as a function of annealing temperature, respectively. Since the thicknesses of the nitride films were changed by annealing at 900 °C for 50 min.
thermal annealing, the areal density of paramagnetic defects is plotted in Fig. 4(a). The paramagnetic defect density and g value did not change after isothermal annealing at 400 °C for 1600 min. As shown in Fig. 1, almost no H₂ desorption was detected at 400 °C. From these results, it is revealed that there were no significant changes in H-related chemical bonds and in the atomic structure of K₀ centers at 400 °C.

Isothermal annealing at 750 and 900 °C for 50 min slightly decreased the paramagnetic defect density, as shown in Fig. 4(a). However, 78% of the paramagnetic defects remained even after annealing at 900 °C for 500 min. Many of K centers were stable up to 900 °C. As shown in Fig. 4(b), the g value was changed by annealing at 750 and 900 °C for 50 min and reached 2.0024 after annealing at 900 °C for 500 min. The nitride films shrank and densified with annealing at 900 °C, as shown in Fig. 2(b). Such shrinkage of the films would have been accompanied by significant changes in the atomic structure. Yan et al. calculated that the g value of the K center is 2.0022 when the central Si atom has an unpaired electron and is back-bonded to three N atoms, which is changed to be 2.0034 when the central Si atom is back-bonded to two N atoms and a Si atom. The g value of 2.0031 obtained from the nitride film with x = 1.31 before thermal annealing is consistent with their calculation result. It is considered that the change from 2.0031 to 2.0024 in the g value shown in Fig. 4(b) was caused by the replacement of a back-bonded Si atom to an N atom. When N–H and Si–H bonds are present at the first or second nearest neighbor sites relative to the central Si atom, ΔHpp would broaden due to hyperfine interactions rather than changing the g value. After thermal annealing at 900 °C for 500 min, ΔHpp did not narrow but broadened from 1.24 to 1.43 mT despite the dissociation and desorption of H atoms from the N–H and Si–H bonds, suggesting that H atoms had a relatively small effect on the ESR signal characteristics.

Figure 3(g) shows the ESR spectrum of the nitride film annealed at 1050 °C for 50 min. It is noteworthy that a signal appeared in the nitride film that was not exposed to UV light. After that, UV exposure and ESR measurements were repeated alternately for the nitride film. The ESR signal intensity increased and was saturated with increasing UV radiation dose. The saturated ESR signal is shown in Fig. 3(b). The signal component induced by UV exposure was obtained by subtracting the ESR signal before UV exposure from the saturated ESR signal, and the paramagnetic defect density and g value obtained from the UV-light-induced signal component are plotted in Figs. 4(a) and 4(b). The g value of the signal component was coincident with that obtained from the nitride films annealed at 900 °C and UV irradiated. On the other hand, the paramagnetic defect density substantially decreased by 1050 °C annealing.

Next, we focused on the ESR signal generated by 1050 °C annealing shown in Fig. 3(g). Figure 5 shows the ESR spectra obtained from the nitride film subjected to annealing at 1050 °C. As the annealing time increased from 0 to 700 min, the ESR signal became larger.

Figures 6(a) and 6(b) show the paramagnetic defect density and g value as a function of annealing time. The paramagnetic defect
density increased monotonically, and the g value was changed to 2.0020 with an increase in the annealing time. Subsequently, the nitride film annealed at 1050 °C for 700 min was etched with a hydrofluoric acid solution. Figure 6(c) shows the relationship between the paramagnetic defect density and the thickness of the nitride film remaining after etching. The paramagnetic defect density decreased as the nitride film became thinner, and a linear relationship was found between the defect density and the thickness of the nitride film. From this result, it is clear that paramagnetic defects were present in the nitride bulk. The signals caused by 1050 °C annealing had complicated characteristics with the g values shown in Fig. 6(b), which were not in agreement with those of ESR signals obtained in the previous studies on silicon nitride films. Attempts were made to analyze the signals; however, their origin remained unclear. In order to clarify the atomic structure of the paramagnetic defects responsible for the signals shown in Fig. 5, further studies are required, such as fabricating silicon nitride films in which silicon and nitrogen are replaced with isotopes and measuring ESR for the films.

In summary, H2 desorption was observed above about 600 °C and the first peak in the H2 desorption rate appeared at 880 °C. Thermal annealing at 750 and 900 °C, which correspond to the temperatures within the peak at 880 °C, caused a change in the atomic structure of K centers and a slight decrease in the K center density.

On the other hand, annealing at 1050 °C, which corresponds to the temperature within the second peak at 1180 °C in the H2 desorption rate, resulted in a substantial decrease in the K center density and also led to the generation of paramagnetic defects with unprecedented characteristics in the nitride bulk. Further research will be necessary to investigate the electrical properties of the paramagnetic defects generated by annealing at 1050 °C.

It is known that the density and properties of point defects depend on the growth conditions of nitride films. Another future challenge is to investigate how the density and properties of point defects in nitride films grown under various conditions change due to high-temperature annealing.
IV. CONCLUSIONS

We have studied the influence of high-temperature thermal annealing on K centers in Si-rich silicon nitride films grown using a single-wafer-type LPCVD reactor with the SiH₂Cl₂:NH₃ system at 750 °C.

In the TDS analysis, H₂ desorption from the nitride films was detected above about 600 °C, and two peaks of H₂ desorption rate appeared at 880 and 1180 °C. Thermal annealing at 750 and 900 °C, which correspond to the temperatures within the first peak at 880 °C in the H₂ desorption rate, caused a change in the g value of K centers, which would be due to the change in the atomic structure around K centers. Many of K centers remained after annealing at 750 and 900 °C.

On the other hand, thermal annealing at 1050 °C, which corresponds to the temperature within the second peak in the H₂ desorption rate, resulted in a substantial decrease in the K center density and the generation of paramagnetic defects with unprecedented characteristics in the nitride bulk. Further studies are required to understand the atomic structure and the electrical properties of the defects.

In the manufacturing processes of nonvolatile semiconductor memories, silicon nitride films are often exposed to thermal annealing at high temperatures. The findings in this study are expected to provide important guidelines for the design of the manufacturing processes.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES