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Charge-trapping defects in Cat-CVD silicon nitride films

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Abstract

We show that Cat-CVD silicon nitride films contain more than 10^{19} cm^{-3} nitrogen-bonded Si dangling bonds, similarly to the case for conventional CVD films. However, the charge-trapping behavior of the Cat-CVD films is found to be quite different, in spite of the same origin for the dominant defects. The difference is ascribed to a non-uniform distribution of defects that is strongly depleted near the surface in Cat-CVD films. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicon nitride; Cat-CVD; Metal-oxide-semiconductor structure; Electron paramagnetic resonance

1. Introduction

Silicon nitride (SiN_x) prepared by low-temperature Cat-CVD (catalytic-chemical vapor deposition) shows a good electrical insulating property which is comparable to high-temperature CVD films [1]. In view of its application to passivation of high-speed GaAs devices, it is important to characterize charge-trapping defects in the films [2]. The fixed charges of defects greatly affect the device performance through modification of the electric-field distribution in devices. In a wide variety of conventional SiN_x films prepared either by plasma-enhanced CVD (PECVD) or low-pressure CVD (LPCVD), a high density ($>10^{18}$ cm^{-3}) of charge-trapping defects were commonly observed [3,4]. However, no measurements on charge-trapping defects have been reported for Cat-CVD SiN_x. Thus, in this report, charge-trapping defects in Cat-CVD SiN_x films are studied and also comparison with those of conventional PECVD SiN_x films.

2. Sample preparation and experimental

Our deposition system was described in a previous report [5]. The deposition parameters were optimized to obtain the highest growth rate (7.5 nm/min) for mass-production. Cat-CVD SiN_x films were deposited using the process conditions given in Table 1. We also prepared a conventional PECVD SiN_x film with the same gas source and similar growth temperature. Both films were nearly stoichiometric (N/Si = 1.1:1.2) and free from oxygen (<0.1 at.%). The hydrogen contents were 11 and 23 at.% for the Cat-CVD and PECVD films, respectively [5]. In these films, no metal impurities were detected by SIMS measurements.

In order to study the charge-trapping behaviors, we made double dielectric Si-MOS (metal oxide semiconductor) samples (Fig. 1). The thin thermal-SiO_2 layer enables capacitance–voltage (*C–V*) analysis without disturbance from the insulator/Si interface states. The areal density of the fixed charge was estimated from shifts in the so-called midgap voltage of 1-MHz *C–V* curves. We

Table 1
Cat-CVD conditions

Parameters	Set points
Catalyzer temperature	1700°C
Catalyzer-wafer distance	75 mm
Substrate temperature	308°C
NH_3 flow rate	200 sccm
SiH_4 flow rate	1.2 sccm
Gas pressure	20 Pa

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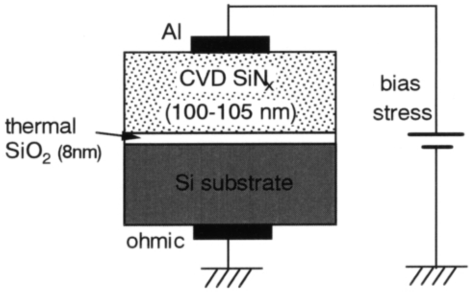

Fig. 1. Si-MOS capacitor structure and configuration for carrier-injection experiments.

carried out carrier-injection experiments by applying a bias stress to the capacitors (see Fig. 1). The bias stress was set to be 60 and 40 V for the Cat-CVD and PECVD samples, respectively, to avoid dielectric breakdown of the capacitor and to maximize the midgap-voltage shift.

Electron paramagnetic resonance (EPR) was used to identify the origin of the charge-trapping defects. EPR spectra were taken with a JEOL X-band spectrometer using 0.4-mT modulation at 100 kHz, a microwave power of 0.01 mW, and a temperature of 20 K. The metal parts of the MOS samples were removed for EPR measurements. Furthermore, cleaved edges of the Si substrates were etched by alkali solutions. This process completely eliminated an undesirable EPR signal of $g = 2.0055$ which arises from Si dangling bonds in the edge regions [6]. In etch-back experiments, the defect density was measured by room-temperature EPR measurements.

We also applied ultraviolet (UV) excitation to the samples, using a deuterium lamp (3–7.5 eV). The illumination was provided for 10–30 min at room temperature.

3. Results and discussion

3.1. Carrier-injection experiments

First, the charge trapping in Cat-CVD SiN$_x$ films is studied by carrier-injection experiments on MOS structures. Fig. 2 shows *C–V* results for Cat-CVD MOS capacitors. In as-grown samples, the *C–V* curve for the Cat-CVD film (a dashed line) is quite similar to that for a PECVD film, and a small amount (1×10^{12} cm^{-2}) of positive charges are commonly observed [7].

However, after carrier injection due to a bias stress, a drastic increase in the density of fixed charge is observed in both films. In Fig. 2, the solid line shows *C–V* results measured after a bias stress. As is seen in the figure, a flat-band voltage of the *C–V* curve is significantly shifted, which clearly indicates the generation of a high density of fixed charge. We found that the observed shifts are reversible with respect to stress-bias polarity and the generated charges can be removed by UV excitation. This observation gives clear evidence for charge trapping at point defects. The density of the trapped charge was approximately 6×10^{12} cm^{-2} for both films. The actual density should be even larger, because *C–V* measurements give an average density of the sheet charge which is weighted by the distance from the insulator/Si interface.

The transient behavior for charge trapping is shown in Fig. 3. Both the Cat-CVD and PECVD films reveal similar transient behaviors: the charge trapping is immediately saturated within a period of 1 s, and more than 10% of injected carriers are efficiently captured at the defects. These features are related to the nature of the charge-trapping defects, and are discussed in the following section.

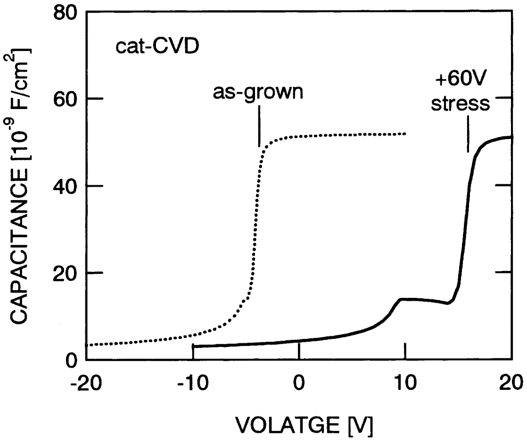

Fig. 2. *C–V* curves for the Cat-CVD SiN$_x$ capacitor.

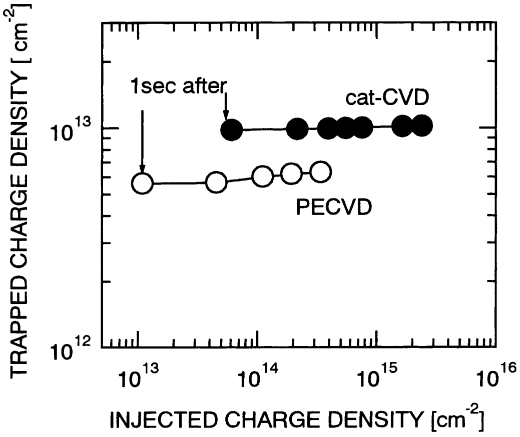

Fig. 3. Transient behavior for charge trapping (Cat-CVD: as-grown → +60 V stress; PECVD: as-grown → –40 V stress). The Cat-CVD film shows the higher density of the trapped charge as compared to the PECVD film, which is due to the increase of positive charge in the as-grown Cat-CVD film [7].

3.2. Origin of charge-trapping defects — the K centers

EPR measurements can reveal the microscopic origin of the defects mainly responsible for the charge trapping in the Cat-CVD films. Fig. 4 shows EPR spectra for (A) as-grown Cat-CVD and PECVD films and (B) for those after UV excitation. As is clear in the figure, UV excitation greatly increases the EPR signal. The spectra (C) show the UV-induced changes [i.e. (B)−(A)], which is clearly dominated by a single broad signal at $g = 2.003$ (solid lines). This signal corresponds to the well-known signal of electrically-neutral K centers. The K center is known as the dominant charge trap in conventional CVD SiN_x films [3], and our study demonstrates that it is also the case for the Cat-CVD films. Based on detailed EPR analyses [4], it is well established that the K centers are nitrogen-bonded Si dangling bonds ($N_3{\equiv}Si$ structure). We point out that the K signal is broader in the Cat-CVD films (2.7 mT) as opposed to the PECVD films (1.9 mT). This might reflect different environments of the K centers in Cat-CVD SiN_x.

The *C–V* and EPR results are consistently explained based on the ‘negative-*U*’ nature of this defect. The apparent absence of net charge in the as-grown films means that the defect occupation is stabilized by nearly equal numbers of negatively- and positively-charged K centers which are both diamagnetic [3]. However, such charged K centers are converted to metastable neutral (paramagnetic) centers by UV excitation [3], resulting in increased EPR signal together with the removal of trapped charge. The transient behavior is also consistent with the nature of the K centers, because the Coulomb attraction of charged K centers can enhance their capture cross-section for injected carriers [3].

In both as-grown spectra (A), a broad resonance at $g = 2.003$–2.006 is commonly observed, which is tentatively attributed to a combination of a neutral K signal ($g = 2.003$) and a Si dangling-bond signal ($g = 2.0055$ [6,8]). We speculate that potential fluctuations and/or unintentional UV irradiation generate metastable neutral K centers in the as-grown films. We also speculate that the $g = 2.0055$ centers are formed in the Si-rich regions of our SiN_x films, because they have a $Si_3{\equiv}Si$ structure [8]. Note that both centers are electrically neutral, which is consistent with the observation of negligible net charge in the as-grown films.

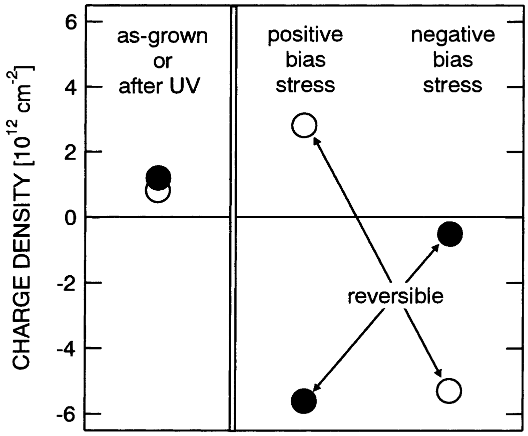

Fig. 5. Relationship between the polarities of bias stress and trapped charge. Solid and open circles are measured for the Cat-CVD and PECVD films, respectively.

3.3. Unusual charge-trapping in Cat-CVD films — non-uniform distribution of the K centers

Although Cat-CVD and PECVD films have the same dominant defects, their charge-trapping behavior was found to be quite different. It appears as a striking contrast in the polarity of the fixed charge (Fig. 5). In PECVD samples, a negative bias stress (= electron injection from the Al side) generates negative fixed charge in the film. This behavior is quite reasonable,

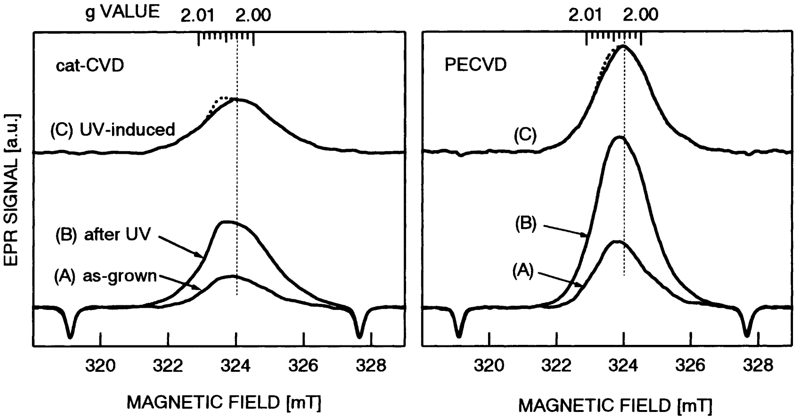

Fig. 4. UV-induced changes in EPR spectra. Two negative lines at both ends are Mn^{2+} marker signals. The spectra were recorded for magnetic field parallel to the [100] axis. The dashed lines indicate a signal from SiO_2–Si interface dangling bonds, which was confirmed by the angular dependence of the *g* factor.

because carrier injection from the Al side is dominant in our MOS capacitors, from a potential barrier due to the thermal SiO_2 layer. Nevertheless, in Cat-CVD films, a negative fixed charge is generated by a positive bias stress, i.e. electron injection from the Si side (Fig. 5). Namely, the charge trapping was largely suppressed for carrier injection from the Al side. It means that the K centers are strongly depleted near the surface of Cat-CVD films. In contrast, in the PECVD films, the K centers appear to be rather uniformly distributed across the thickness. With stronger bias stresses (~60 V), compensation of net charge was observed pronouncedly for the PECVD samples. This indicates that the charge trapping in the PECVD films took place rather symmetrically from both the Al and Si sides. In both films, positive fixed charge is appreciably compensated by negative charge generated in the opposite side of the film (see Fig. 5). We speculate that this is due to low injection efficiency for holes as compared to electrons.

To confirm the defect distribution across the thickness, we performed etch-back experiments using buffered HF (BHF) treatments. BHF-etching rates were approximately 0.15 and 0.76 nm/s for Cat-CVD and PECVD films, respectively, which were measured by the spectroscopic ellipsometry. Before etching, the samples were excited by UV light to neutralize the K centers completely. Then, we measured the reduction in the EPR signal due to etching. These profiles are shown in Fig. 6. Consistent with the charge-trapping behavior, the defect density in the Cat-CVD film is very small in 10 nm thickness from the surface, and becomes larger with close proximity to the substrate. However, PECVD films show a rather uniform distribution, which is in good agreement with their charge-trapping behavior. From the etch-back experiments, total K densities are estimated to be similar for both films: from 1×10^{19} to 2×10^{19} cm^{-3} and from 1×10^{14} to 2×10^{14} cm^{-2}, respectively. The number of the K centers is large enough to account for the fixed charge densities observed in Figs. 2 and 3. These values agree with typical figures (10^{18}–10^{19} cm^{-3} [3]) for various conventional CVD films.

4. Summary

The charge-trapping defects in Cat-CVD SiN_x have been studied by means of C–V and EPR analyses. We found that Cat-CVD films contain K centers ($N_3{\equiv}Si$ defect) as a dominant defect, in a manner similar to the conventional CVD SiN_x films. The *C–V* and EPR results were consistently interpreted in terms of negative-*U* behavior of the K centers. The unusual charge trapping was observed for Cat-CVD films, and is attributed to the non-uniform distribution of the K centers in the films.

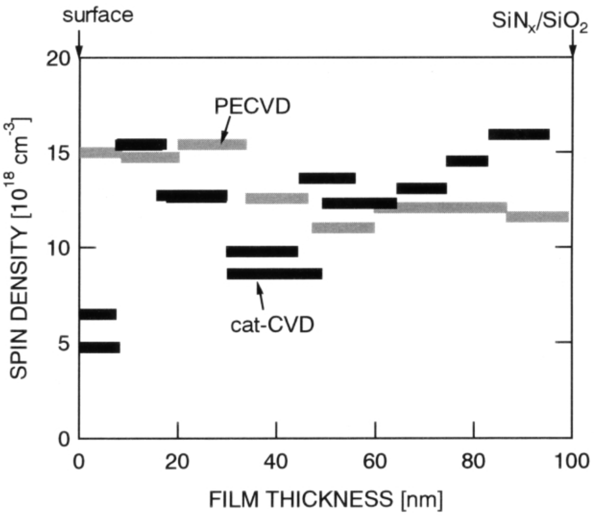

Fig. 6. Defect density profiles estimated by etch-back experiments.

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