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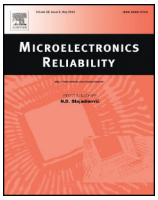

Mechanism of gate dielectric degradation by hydrogen migration from the cathode interface

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ABSTRACT

Hydrogen migration in a SiO_2/Si system is examined in detail by nuclear reaction analysis. Electrical reliability measurements reveal a correlation between hydrogen migration from the cathode interface to the SiO_2/Si interface and dynamic degradation of the gate dielectric. In addition, the defect levels generated in the bulk of SiO_2 have an energy distribution corresponding to that of oxygen vacancies, as revealed by comparing the measured and simulated stress-induced leakage current. Finally, a model of hydrogen-induced gate dielectric degradation is proposed based on first-principles calculations.

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1. Introduction

The reliability of gate dielectrics, which suffer from problems such as time-dependent dielectric breakdown, negative bias temperature instability (NBTI) and hot carrier injection (HCI), has been a critical problem for the scaling of devices such as logic transistors, analog transistors, and power transistors. The relationship between dielectric degradation and hydrogen has been a subject of controversy, and various arguments have been advanced [1–6]. A typical example is the hydrogen release model, which explains the phenomena of gate dielectric breakdown and stress-induced leakage current (SILC) [1–4]. In this model, tunneling hot electrons release hydrogen from the anode interface regardless of the bias polarity, leading to degradation both at the SiO_2/Si interface and in bulk SiO_2. Furthermore, degradation due to HCI is also thought to be triggered by interfacial hydrogen at the SiO_2/Si interface [5]. Recently, hydrogen release model on the gate side was reported to describe the origin of permanent NBTI degradation [6]. Therefore, it is necessary to conduct detailed analysis of the change in the depth profile of hydrogen in the dielectrics between the upper interface with the gate electrode and the lower interface with the Si substrate in order to discuss the relationship between hydrogen and gate dielectric degradation.

Nuclear reaction analysis (NRA) using the $^{1}H(^{15}N, \alpha\gamma)^{12}C$ reaction with a resonance energy of 6.385 MeV is an effective method for analyzing hydrogen profiles in the SiO_2/Si system because the resonance width is sufficiently narrow (1.85 keV) compared with the stopping power (1.684 keV/nm) of SiO_2 [7–10]. In actuality, the depth resolution is mainly determined by a Doppler effect induced by the zero-point vibration of H atoms and the straggling effect. The Doppler effect can be effectively reduced by increasing the incident angle of the $^{15}N^{2+}$ ion beam, leading to improvement of the effective depth resolution. For example, the effective depth resolution is about 7 nm at a depth of 25 nm with an incident angle of 60° from the surface normal of a SiO_2 specimen. In addition, unlike secondary ion mass spectrometry (SIMS), NRA enables accurate estimation of the amount of hydrogen even at material interfaces, without the matrix effect. In some studies, hydrogen migration was observed in NRA measurements, forming the basis of the argument that dielectric reliability and hydrogen migration are related [11–13]. At the beam energies of around 6 MeV, electron stopping power is dominant compared with the nuclear stopping power. Liu et al. pointed out that the secondary electrons generated by $^{15}N^{2+}$ ion beam irradiation cause hydrogen detachment from various binding sites followed by migration, and they then proposed that the transport behavior of hydrogen can be explained by the same mechanism, regardless of whether it is caused by secondary electrons under $^{15}N^{2+}$ ion beam irradiation or by energetic carriers under electrical stress [11]. In fact, they confirmed that the increase in hydrogen concentration at

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the SiO_2/Si interface under electrical stress of −5 MV/cm at 360 °C for 6 h closely resembles the increase under $^{15}N^{2+}$ ion beam irradiation. However, they have not reported the relationship between the generation of bulk defects under high-field Fowler-Nordheim tunneling (FN) electrical stress and hydrogen migration. Recently, we found a relationship between hydrogen migration due to electrical stress and that due to $^{15}N^{2+}$ ion beam irradiation in nMOSFETs (*n*-type metal–oxide–semiconductor field-effect transistors), and confirmed that the increase in both the interface defect density (D_{it}) and gate leakage current were caused by the hydrogen migration in the SiO_2/Si system [12].

In this paper, we focus on the relationship between dielectric degradation under high-field FN electrical stress and hydrogen migration. We report a detailed analysis of hydrogen migration and its correlation with electrical reliability in the SiO_2/Si system. We also characterize the energy distribution of defect levels generated in the bulk of SiO_2 by comparing electrical measurements and simulations of SILC. Finally, we discuss the mechanism of dielectric degradation based on hydrogen migration in bulk SiO_2 and at the interface based on first-principles calculations.

2. Experiment and theoretical methods

To investigate hydrogen migration precisely, we used Al (10 nm)/SiO_2 (25 nm)/Si specimens. First, SiO_2 was thermally grown on a *p*-type Si substrate to prepare the stack with a relatively low amount of hydrogen. To observe the hydrogen migration within the detection limit of NRA, we exposed specimens to air before the metal evaporation and made a rich hydrogen source at the Al/SiO_2 interface. We annealed some specimens at 250 °C and 400 °C in an O_2 atmosphere and transported them in the metal evaporation apparatus as quickly as possible in order to minimize the amount of the adsorbed hydrogen at the Al/SiO_2 interface. Then the Al layer was deposited. The size of Al area for NRA specimen is 1×1 cm^2. Fig. 1 shows a schematic of the NRA method for obtaining the hydrogen depth profile. The specimen was irradiated by an $^{15}N^{2+}$ ion beam with beam energies higher than the resonance energy in order for a nuclear reaction to occur at a desired depth that is exactly defined by the energy loss in the Al/SiO_2 layer due to the stopping power of the Al and SiO_2. The hydrogen depth profile was then obtained from the γ-ray yield as a function of the incident energy of the $^{15}N^{2+}$ ion beam. On the other hand, the ion dose dependence at a desired depth corresponding to a fixed energy can be obtained by varying the $^{15}N^{2+}$ ion beam dose at the fixed beam energy. In NRA measurements, it is important to pay careful attention to and control unexpected hydrogen migration due to the $^{15}N^{2+}$ ion beam as described in the Section 1. Therefore, we have developed a high-resolution NRA system by installing an anticoincidence trigger system and an automatic sample positioning system as described elsewhere [13]. The background level corresponding to a hydrogen concentration of 3×10^{19} atom/cm^3 in SiO_2 was achieved at a beam current of 50 nA with this system.

To reveal the mechanism of dielectric degradation by hydrogen, the change in the hydrogen depth profile caused by electrical stress should be observed. However, it is difficult to apply a high-field FN electrical stress to a specimen with a gate area of 1×1 cm^2 as defined by the beam size of NRA on the sample, because dielectric breakdown occurs before the electrical stress is applied for a sufficiently long time to cause migration of hydrogen as much as 3×10^{19} atoms/cm^3 that can be detected by NRA. After the breakdown occurs, the high voltage and the high electric field stress cannot be applied because of the leak current. Therefore, it was difficult to obtain the hydrogen concentration before and after application of the high-field electrical stress in order to investigate the generation mechanism of the bulk defects. As described in the Section 1, hydrogen migration under $^{15}N^{2+}$ ion beam irradiation is thought to be related to that under electrical stress [11–13]. Moreover, the hydrogen concentration in the bulk SiO_2 and at the SiO_2/Si interface increases with increasing ion dose as a result of hydrogen migration. Therefore, to analyze the relationship between dynamic hydrogen migration and gate dielectric degradation in detail, we measured the hydrogen depth profiles by varying the $^{15}N^{2+}$ ion dose.

Standard high-frequency capacitance-voltage (C-V) measurements [14–16]. were used to obtain both the interface defect density and the bulk defect density. The capacitor specimens were processed on the same wafer and at the same time as the NRA specimens. The gate size is 100×100 μm^2. A negative gate bias stress with a gate electric field of $E_{ox} = -8$ MV/cm, which is FN stress, was applied to the capacitor specimens for 1000 s at room temperature. Then, the interface defect density (D_{it}) was measured from the C-V stretch-out compared with the ideal C-V curve [14]. The bulk defect density (N_t) was measured from the flat-band voltage shift (ΔV_{fb}). To distinguish these two types of defects, the contribution of the voltage shift caused by the interface defect density was estimated and subtracted from the total flat-band voltage shift.

We determined the energy level of defects in bulk SiO_2 by comparing electrical measurements and simulations of SILC in nMOSFETs. For the specimen with the thick gate oxide of 25 nm, the SILC could not be clearly observed because the leakage current was lower than the detection limit. Therefore, we used a specimen with thinner gate oxide of

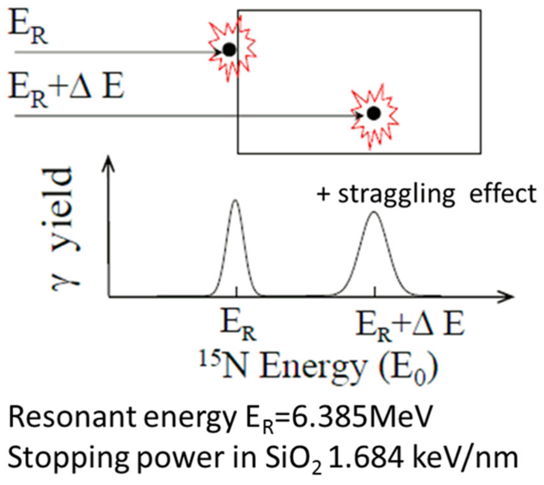

Fig. 1. Schematic of estimation method for obtaining the hydrogen depth profile [8].

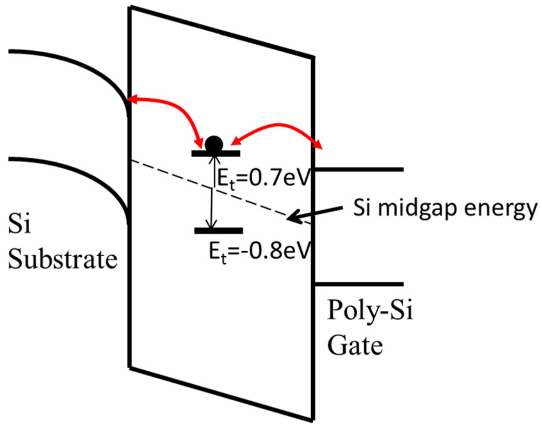

Fig. 2. Schematic of the SILC simulation model. Two typical defect levels are shown in the figure: the upper level is an oxygen vacancy (V_O) in a fully relaxed, doubly occupied (i.e., negatively charged) state (V_O^{1-}), and the lower level is a Si-DB ((E'-center)$^{1-}$). The details are provided in Section 3.2.

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