Investigation of the Possible Origins of Lattice Distortion at the Surface of Thermally-Oxidized 4H-SiC (0001) based on the Physical Analysis of Remained Byproducts

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Abstract

The possible origins of lattice distortion at the surface of thermally-oxidized 4H-SiC (0001) were investigated. Kinetics of lattice relaxation suggest that the existence of byproducts remained in 4H-SiC after thermal oxidation could be considered as one of the possible origins. The physical analysis using TDS and FTIR on both thermallyoxidized and ion-implanted samples suggests that oxygen plays an important role to cause significant distortion.

1. Introduction

One of the unique advantages of 4H-SiC compared to other wide band-gap semiconductors materials is the ability to form SiO₂ layer by thermal oxidation. The formation of thermally-oxidized SiO₂/4H-SiC interface has been reported to induce macroscopic distortion due to the bending of SiC wafer [1]. In addition to the macroscopic one, recently, we reported oxidation-induced lattice distortion locally at the surface region of 4H-SiC caused by the formation of SiO₂/4H-SiC interface [2]. However, the origin of such significant distortion has not been clarified yet.

In this report, we investigated the possible origins of anomalous lattice distortion at the surface of thermallyoxidized 4H-SiC (0001) based on the physical analysis of remained byproducts, studied by the kinetics of lattice relaxation, Fourier-transform infrared spectroscopy with attenuated total reflectance mode (FTIR-ATR), and thermal desorption spectroscopy (TDS) analysis.

2. Experimental Methods

4° off-axis 4H-SiC (0001) wafers with 5 μ m-thick n-type doped (~1 × 10¹⁶ cm⁻³) epitaxial layers were used as substrates. Dry oxidation in 1-atm-oxygen (O₂) gas was performed at 1300°C. Annealing were then performed in 1atm-Ar at 1150, 1300, or 1400°C for various time after total oxide removal in diluted hydrogen fluoride (HF) solution. For other samples, O and Ar ion implantation were performed at the dose of 10¹⁵ atoms/cm² at 15 and 35 keV, respectively. All samples were characterized by in-plane XRD with shallow incident angles from 0.23° to 1.25°. TDS and FTIR analysis were performed to investigate the desorbed molecules from the surface of 4H-SiC and the possible structure that cause distortion, respectively.

3. Results and Discussion

Thermal oxidation induces lattice distortion at the surface of 4H-SiC (0001), observed as the increase of $(1\overline{1}00)$ interplanar spacing, $d_{(1\overline{1}00)}$ [2]. Fig. 1(a) and (b) show

annealing time dependence of the changes of lattice distortion (D, increase ratio of $d_{(1\overline{1}00)}$) and temperature dependence of lattice relaxation rate constant (k), respectively. The Ar annealing for longer time and higher temperature induce more relaxation on the lattice structure of 4H-SiC surfaces [3]. Fig. 1(a) shows that the changes of D are not linearly correlated to the annealing time. We found that the lattice relaxation process seems to follow the second order rate law, because the changes of inverse of $D(D^{-1})$ as a function of annealing time show good linearity (data not shown). From the temperature dependence of the relaxation rate constant (Fig. 1(b)), the estimated activation energy of around 1 eV was obtained, suggests that it might be related to a bond rearrangement or movement process with a relatively low activation energy. We speculated that one of the possible origins of lattice distortion would be the formation of a certain byproducts to be remained at the surface of 4H-SiC wafer after oxidation, while the relaxation might involve the movement of that byproducts then desorbed out from the surface of 4H-SiC [3].



Fig. 1(a) Annealing time dependence of the changes of lattice distortion (*D*) at the surface of thermally-oxidized 4H-SiC and (**b**) temperature dependence of lattice relaxation rate constant (k).



Fig. 2(a) Penetration depth dependence of $d_{(1\bar{1}00)}$ of thermallyoxidized and ion implanted 4H-SiC (0001) and (b) Ar annealing time dependence of the changes of lattice distortion (*D*).

The similarity and difference between the impact of thermal oxidation and ion implantation on the lattice structure of 4H-SiC were then investigated. **Fig. 2(a)** shows the penetration depth dependence of $d_{(1\bar{1}00)}$ of thermally-oxidized sample with ~30 nm-thick SiO₂, O-implanted samples and Ar-implanted samples at the dose of 10^{15} atoms/cm². Ar-implanted sample shows much more significant distortion than O-implanted sample and almost the same as that induced by thermal oxidation to form ~30 nm-thick SiO₂. Since ion bombardment generates interstitial atoms (and vacancies) in the crystals [4] and heavier ions tend to cause higher amount of them, it seems that large number of interstitials atoms at surface region of 4H-SiC could be considered as one of the possible origins of the distortion on the as-implanted samples.

However, a clear contrast between Ar- and O-implanted samples are observed when we investigated the effect of Ar annealing on the lattice structure of 4H-SiC. Annealing at the temperature of 1300°C was performed after total oxide removal in diluted HF. Annealing time dependence of lattice distortion on Ar-implanted, O-implanted, and thermallyoxidized 4H-SiC samples are shown in Fig. 2(b). Annealing resulted in partial lattice relaxation on Ar-implanted and thermally-oxidized 4H-SiC (note that the lattice of Arimplanted sample is more difficult to be relaxed). On the other hand, annealing for 10 min induces much more significant lattice distortion on O-implanted sample. Our speculation of this significant increase is the possibility of oxygen invasion into 4H-SiC lattice, since annealing could induce the migration of interstitial atoms. The more significant distortion at the surface of O-implanted sample should be induced mainly by the O-related structure in the lattice (for example: Si-O-C structure), not by the interstitial atoms generated by ion bombardment as expected in Arimplanted sample. CO

Fig. 3 Schematic illustration of lattice distortion introduction by invading oxygen atoms and lattice relaxation at the surface of 4H-SiC.



Kinetics of lattice relaxation suggest that the existence of byproducts remained in 4H-SiC after oxidation could be considered as one of the possible origins, while implantation results suggest that oxygen plays an important role to induce significant distortion at the surface of 4H-SiC. We speculated that the formation of defects like Si-O-C structures [5] to be remained inside 4H-SiC crystal by oxidation and the decomposition of those structures by movement of those invading oxygen atoms and emitted out as CO would be the possible causes of the lattice distortion introduction and lattice relaxation of thermally-oxidized 4H-SiC, respectively, as illustrated in **Fig. 3**.

TDS and FTIR analysis were then performed to support our consideration. **Fig. 4(a)** shows the FTIR spectra of 4H-SiC sample before and after oxidation/implantation, measured with ATR mode using Ge prism with 45° incidence angle. FTIR spectra of the oxidized/implanted sample shows in common, the absorption at the wavenumber of around 840, and 1540 cm⁻¹, whereas the wafer before 1295 oxidation/implantation does not show the peaks in those wavenumbers. Those peaks are related to Si-O bending, C-O stretching, and conjugated C=O asymmetric stretching vibration [6], respectively, suggesting that oxygen remained in 4H-SiC after oxidation and oxide removal. TDS was then performed for the 4H-SiC samples before and after oxidation (after oxide removal) in isotope ¹⁸O₂ ambient (0.7 atm) at 1300°C for the sensitivity improvement. In this TDS analysis, oxygen concentration in 4H-SiC was detected as $C^{18}O(m/z)$ 30) desorption. TDS results shown in Fig. 4(b) describes that the high intensity peak attributed to C18O desorption was observed only on thermally-oxidized sample, indicating the existence of oxygen inside 4H-SiC after oxidation. These results support our proposed mechanism that the lattice distortion was induced by oxygen invasion into 4H-SiC crystal during thermal oxidation, while the relaxation involves the migration of that invading oxygen, then emitted as CO molecule.



Fig. 4 (a) FTIR-ATR spectra of thermally-oxidized and implanted 4H-SiC and (b) TDS spectra of $C^{18}O$ as a measure of oxygen concentration in 4H-SiC. The data for the as-received wafer are also shown for comparison in both (a) and (b).

4. Conclusions

We investigated the possible origins of lattice distortion at the surface of thermally-oxidized 4H-SiC (0001). Kinetics of lattice relaxation suggest that the existence of byproducts remained in 4H-SiC after oxidation should be considered as one of the possible origins, while implantation results suggest that oxygen plays a key role to induce significant distortion. The lattice distortion is possibly caused by the oxygen invasion into 4H-SiC lattice and forms some structures (like Si-O-C) to be remained inside 4H-SiC after thermal oxidation, while the decomposition of those structures by movement of the invading oxygen atoms and their ejection as CO would be one of the possible mechanisms of the lattice relaxation.

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