Recovery of Local Lattice Distortion at the Surface of Thermally-Oxidized 4H-SiC (0001) by Post-Oxidation Annealing

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Abstract

Recovery of thermal-oxidation-induced local lattice distortion at 4H-SiC surface by post-oxidation annealing was studied. The lattice distortion could be partially recovered by Ar, NO, and H₂O annealing, possibly due to the removal of accumulated oxidation-induced defects. Kinetics study suggested that recovery process involves the emission of CO molecule that induced by the migration of invading oxygen inside 4H-SiC crystal.

1. Introduction

Formation of SiO₂ layer by thermal oxidation is a unique advantage of 4H-SiC compared to other wide band-gap semiconductors materials. Macroscopic distortion due to the bending of 4H-SiC wafer induced by formation of thermallyoxidized SiO₂/4H-SiC interface has been studied [1]. In addition to such macroscopic one, we have also reported the oxidation-induced distortion locally in the vicinity of the interface [2]. One possible origin of this distortion is oxidation-induced interstitial atoms in the surface region in a proposed oxidation mechanism [3]. However, the recovery of that surface lattice distortion hasn't been clarified yet.

In this report, we investigated the recovery of local lattice distortion at the surface of thermally-oxidized 4H-SiC (0001) Si-face by post-oxidation annealing in Ar, NO, and H₂O, directly from the changes in interplanar spacing of 4H-SiC crystal characterized by in-plane X-ray diffractometry (XRD).

2. Experimental Methods

N-type doped ($\sim 1 \times 10^{16} \text{ cm}^{-3}$) 4H-SiC (0001) epitaxial wafers with 4° off-axis were used as substrates. Dry oxidation at 1300 °C for various time were performed, followed by post-oxidation annealing in O2 at 800 °C for 30 min. For several samples, thermally-grown SiO2 layer were then gradually removed by using buffered hydrogen fluoride (BHF) solution for various etching time. Post-oxidation Ar annealing processes were performed at 1150, 1300, and 1400 °C for various time after oxide removal in diluted HF. NO annealing (in 33% NO diluted by N2) at 1150 °C for 2 hr and H_2O annealing (in 90% $H_2O + 10\% O_2$) at 800 °C for 8 hr, were also done for comparison. All samples were characterized by in-plane XRD to determine the interplanar spacing of lattice planes perpendicular to the wafer surfaces. The shallow incident angles from 0.23 to 1.25 degree were employed to limit the X-ray penetration depth from around 5 nm to 1.5 µm. Thermal desorption spectroscopy (TDS) analysis was done to investigate the desorbed molecules from the surface of 4H-SiC.

3. Results and Discussion

Lattice distortion at the surface of thermally-oxidized 4H-SiC (0001) was observed as the increase of $(1\overline{1}00)$ m-face interplanar spacing, $d_{(1\overline{1}00)}$. Since the lattice distortion exists locally at the surface region, the remaining defects of thermal oxidation would be considered as the origin of this lattice distortion [2]. **Fig. 1** shows the relationship between D (increase ratio of $d_{(1\overline{1}00)}$) and oxidation time, together with schematic illustration of defect-induced lattice distortion at the surface of thermally-oxidized 4H-SiC. The larger lattice distortion time might be induced by the larger amounts of defects generation.



Fig. 1 Relationship between D and oxidation time, together with the schematic illustration of defect-induced lattice distortion at the surface of 4H-SiC.



Fig. 2(a) The changes in penetration depth dependence of $d_{(1\overline{1}00)}$ of 4H-SiC with and without SiO₂ by Ar annealing and (b) comparison between Ar and NO annealing on the lattice recovery.

The lattice distortion could not be recovered by SiO_2 removal alone [2], thus the possibility of lattice recovery was then investigated by performing post-oxidation annealing in Ar at 1300 °C. **Fig. 2(a)** shows recovery of the distorted lattice at 4H-SiC surface with and without SiO₂ layer. It

shows that annealing process could significantly recover the distorted lattice, regardless of the existence of SiO₂ layer. However, recovery of the distorted lattice was faster on the 4H-SiC sample without SiO₂ layer. Based on our consideration that the surface distortion would be the result of defect formation, these post-oxidation annealing processes should cause the migration and removal of those accumulated defects in the surface region. Therefore, we speculated that the existence of SiO₂ layer might limit the removal of accumulated defects from the surface of 4H-SiC and resulted in slower recovery process, especially at the shallow region.

Comparison of the impact of Ar and NO annealing on the lattice recovery was shown in **Fig. 2(b)**. Both Ar and NO annealing at 1150 °C could partially reduce the lattice distortion, while the impact was almost the same between the two processes, when the SiO₂ layer remain on the top of 4H-SiC. Furthermore, annealing process of the oxidized 4H-SiC samples without SiO₂ layer resulted in faster recovery, where the Ar annealing shows more significant impact than NO annealing. Based on our consideration above, we speculated the slower lattice recovery in NO was induced by the existence of additional SiO₂ layer formed during nitridation process. This slower recovery might also be induced by additional oxygen invasion from NO molecules into 4H-SiC structure.



Fig. 3 Annealing time dependence of inverse of D. Annealing temperature (T) dependence of recovery rate constant (k) was also shown in the inset.

Next, we investigated the kinetics of lattice recovery process induced by Ar annealing. Post-oxidation Ar annealing for various time were done at different temperature in order to estimate the activation energy (E_a) of the recovery process. We tried to fit the results into several rate laws, including power law, first, and second order rate law. Then we found that the recovery process seems to follow the second order rate law. Since the recovery rate was proportional to the square of D, plot of 1/D vs annealing time shows good linearity, as shown in **Fig. 3**. The obtained E_a of the recovery process of ~ 0.94 eV suggests that the recovery process is limited by a bond rearrangement or migration process with a relatively low activation energy. One of the possible processes would be the CO emission and migration from Si-O-C structure in 4H-SiC crystal, considering the theoretically predicted energies in Ref. [4], if we assume that such defects are introduced by invading oxygen during thermal oxidation.



Fig. 4 The effect of H₂O annealing on (a) penetration depth dependence of $d_{(1\bar{1}00)}$ of dry-oxidized 4H-SiC and (b) TDS of C¹⁸O as a measure of oxygen concentration in 4H-SiC. No TDS peak was observed for the before oxidation 4H-SiC sample.

The effect of H_2O annealing (in 90% $H_2O + 10\% O_2$) at 800 °C on the lattice recovery was then investigated. Fig. 4(a) shows that H₂O annealing could partially recover the distorted lattice, especially at the shallow region. Based on our proposed recovery mechanism, H₂O annealing should also induce oxygen-related defects removal from the inside of 4H-SiC structure. In order to confirm that possibility, TDS analysis was done for the oxidized 4H-SiC samples with and without H₂O annealing. In this TDS analysis, oxygen concentration in 4H-SiC was detected as CO. For the sensitivity improvement of CO detection, ¹⁸O₂ and H₂¹⁸O were employed in the samples preparation, and $C^{18}O$ (m/z = 30) desorption was then investigated. TDS results shown in Fig. 4(b) describes that the peak intensity attributed to $C^{18}O$ desorption was lower on H₂O-annealed sample, compared to the sample without H₂O annealing, indicating the lower amount of invading oxygen inside the H₂O-annealed sample. This result supports our proposed mechanism that the lattice distortion was induced by oxygen invasion into 4H-SiC crystal during thermal oxidation, while the lattice recovery involves the migration of that invading oxygen, then emitted from the inside of 4H-SiC crystal as CO molecule.

4. Conclusions

The recovery process of local lattice distortion at surface of thermally-oxidized 4H-SiC (0001) could be done partially by Ar, NO, and H₂O annealing. One possible reason of this recovery is the migration of invading oxygen and emitted as CO molecule from the inside of 4H-SiC. Even though the clarification of the origin of such anomalous distortion in the surface region needs further investigation, our results revealed that both oxidation and annealing processes should have a significant impact on the 4H-SiC surface structure and its quality.

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