Atomistic characterization of radical nitridation process on Si(100) surfaces

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Introduction

Si ULSI technology has advanced by scaling the device dimensions of metal-oxide-semiconductor field-effect transistors (MOSFETs). This has given rise to a historical trend of reducing a thickness of gate dielectric films and, in recent years, the SiO_2 gate film with a thickness less than 2 nm is seriously required. The devices with these thin gate films must postulate the high reliability which is often evaluated by leakage current and time-dependent dielectric breakdown characteristics of the films. However, it is difficult to meet these requirements by using thin SiO_2 films as the gate films since a direct tunneling current becomes dominant. Recently, in order to solve this problem, insulator materials with a high dielectric constant (high-k) have been actively investigated. Especially, metal oxides such as ZrO_2 or HfO_2 and their silicates have recently attracted much attentions to replace the SiO_2. In this context, the application of silicon nitride to gate insulator films has quite important implication in technological development of MOSFET. This is because it has higher dielectric constant than that of SiO_2 and might be expected to play a role in a diffusion barrier for oxygen and metal atoms during the preparation of the high-k materials on top of it. Furthermore, its higher barrier height for electron emission than those offered by the other high-k materials is useful to construct desirable energy-band-alignment around the gate region in the MOSFET devices.

In spite of those promising natures of silicon nitride, the role of nitrogen atoms and an atomic-scale reaction-process during nitridation of Si surfaces have not been fully understood yet. In this paper, we review our recent studies which aim at clarifying silicon nitride film evolution on an atomic scale during nitridation on Si(001) surfaces.[1-3] The atomistic configuration of the nitrided Si surface at a very initial stage and the resultant silicon nitride film morphology have been thoroughly investigated by scanning tunneling microscopy (STM). In addition, using scanning tunneling spectroscopy (STS), we reveal the relationship between local electronic states of the nitride films and atomistic modification relating to the nitridation reaction.

Initial nitridation process of Si(100)-2×1 surfaces

The initial nitridation process of Si(100)-2×1 clean surfaces has been investigated by STM and STS. The nitridation was carried out by using radical nitrogen formed by discharging molecular nitrogen with a radio frequency of 13.56 MHz and charged species were removed by an ion-trap system. The substrate temperature ranged from 350°C to 850°C.

After exposing the Si clean surface to the radical-nitrogen of about 5 Langmuir (L) at a substrate temperature of 350°C, the STM image of the surface showed the increase in the density of bright spots originating from C-type defects and the creation of dark regions due to the existence of nitrides. From the STS analysis for these regions, it is found that both the nitridation and the local detachment of surface atoms occur simultaneously during the radical-nitrogen exposure. These reactions have been also observed at substrate temperatures of 500°C and 850°C. In particular, after the nitridation at a temperature of 850°C with radical-nitrogen exposure of about 1 L, linear defects perpendicular to dimer rows were clearly formed. Furthermore, double dark lines were frequently observed on an atomic scale in the STM image. STS analysis of these dark-line regions clarified that the initial nitridation reaction occurs preferentially at the backbonds of surface Si atoms. For the stepped Si(100) surface after the nitridation, the dark regions were clearly observed along the step edges in the STM image. This result indicates that the nitridation occurs preferentially at the step on Si(100)-2×1 surfaces.

Temperature dependence of film evolution and electrical property

The growth sequence of silicon nitride films on clean Si(100)-2×1 surfaces has been also examined by STM and STS. The morphology of the film critically depends on the substrate temperature. It is found that the nitridation proceeds in a layer-by-layer manner at substrate temperatures less than 500°C, in which a continuous film is formed by the coalescence of two-dimensional islands. At nitride thicknesses above 0.6 nm, the film is homogeneously formed over the entire surface. On the other hand, at a substrate temperature of 800°C, the nitridation initiates in a manner of island growth. These islands grow preferentially along the <011> direction perpendicular to the Si dimer rows and the nitridation proceeds via lateral growth of the nitride islands. STS spectra obtained from the 0.5-nm-thick nitride islands distinctly showed a bandgap of about 4.0 eV that is very close to the bandgap of bulk Si_3N_4.

Electrical characteristics

We have investigated the electrical characteristics of metal-insulator-semiconductor (MIS) capacitors with nitride films formed at a substrate temperature of 500°C by radical nitrogen. The MIS capacitor with a 5.4-nm-thick nitride film shows low hysteresis of less than 0.1 eV. The leakage current density of the MIS capacitor is less than 1×10^{-6} A/cm^2 at gate voltages of less than -2V. This value is much less than that of SiO_2 with the same film thickness (3 nm) by a factor of 10^{-3}. These electrical properties indicate that the nitride films formed by radical nitrogen are applicable to gate insulators.

References

1) D. Matsushita, H. Ikeda, A. Sakai, S. Zaima, and Y. Yasuda, Thin Solid Films **360**, 293 (2000).
2) D. Matsushita, H. Ikeda, A. Sakai, S. Zaima, and Y. Yasuda, Jpn. J. Appl. Phys. **40**, 2827 (2001).
3) H. Ikeda, D. Matsushita, S. Naito, K. Ohmori, A. Sakai, S. Zaima, and Y. Yasuda, Jpn. J. Appl. Phys. **41**, 2463 (2002).