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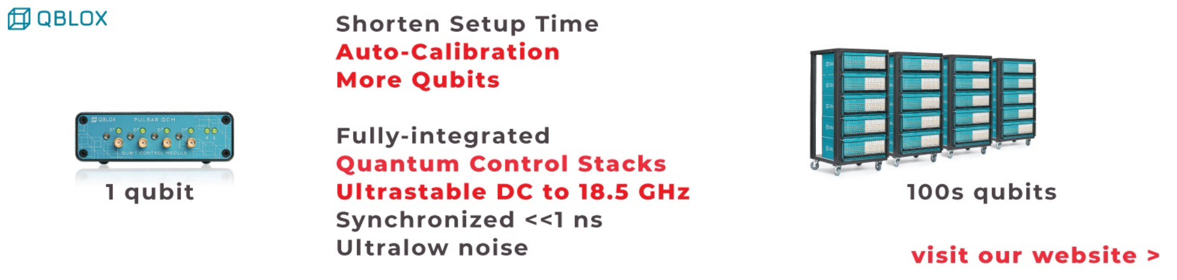

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Humidity-dependent stability of amorphous germanium nitrides fabricated by plasma nitridation

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We have investigated the stability of amorphous germanium nitride (Ge_3N_4) layers formed by plasma nitridation of Ge(100) surfaces using x-ray photoelectron spectroscopy and atomic force microscopy. We have found that humidity in the air accelerates the degradation of Ge_3N_4 layers and that under 80% humidity condition, most of the Ge–N bonds convert to Ge–O bonds, producing a uniform GeO_2 layer, within 12 h even at room temperature. After this conversion of nitrides to oxides, the surface roughness drastically increased by forming GeO_2 islands on the surfaces. These findings indicate that although Ge_3N_4 layers have superior thermal stability compared to the GeO_2 layers, Ge_3N_4 reacts readily with hydroxyl groups and it is therefore essential to take the best care of the moisture in the fabrication of Ge-based devices with Ge_3N_4 insulator or passivation layers. *© 2007 American Institute of Physics*. [DOI: 10.1063/1.2799260]

The aggressive scaling of Si-based metal-oxide-semiconductor field effect transistors (MOSFETs) has been accompanied by the investigation of new technologies to improve device performance, such as metal/high-*k* gate stacks and strained channels. Germanium (Ge) has recently attracted tremendous attention from those searching for new channel materials because its hole and electron mobilities are higher than those of Si.[1,2] It has been reported, however, that Ge is oxidized to form unstable GeO_x during deposition and annealing processes. The poor stability of GeO_x layers results in the degradation of MOS devices and also hinders the integration of high-*k* gate dielectrics with Ge channels. Since nitrogen incorporation into the Ge oxides is supposed to provide higher dielectric constant and improve stability, Ge_3N_4 is expected to be utilized not only as a buffer layer for high-*k* dielectrics grown on Ge substrates but also as a gate insulator itself for Ge-based FETs. While it has been reported that oxygen-free pure Ge_3N_4 films are hard to fabricate by conventional chemical vapor deposition and thermal nitridation of Ge surfaces, Maeda *et al.* have shown that pure Ge_3N_4 films can be fabricated by using nitrogen radicals to nitride Ge surfaces.[3]

Recently, we succeeded in the fabrication of pure Ge_3N_4 layers by utilizing high-density nitrogen plasma and investigated thermal stability of the nitrided layer under vacuum or in a nitrogen ambient for Ge-based device application.[4] Our x-ray photoelectron spectroscopy (XPS) study clearly demonstrated both selective thermal decomposition of the GeO_2 layers and superior thermal stability of Ge_3N_4 layers up to 550 °C. Moreover, we found that oxidation of the Ge_3N_4 surface occurred after air exposure even at room temperature. This suggests the effects of moisture, that is, hydroxyl groups on the surface oxidation of Ge_3N_4, which is consistent with the results of a previous study showing that the hydroxyl groups in water vapor enable oxygen to break the Ge–Ge backbonds in halogen-terminated Ge surfaces exposed to air.[5] However, due to the lack of basic research on the Ge_3N_4 films, these contradictions on the surface reactivity are not understood yet. From this point of view, in this work, we have studied humidity-dependent stability of Ge_3N_4 layers and propose a reaction model for the nitride surfaces.

The starting substrates are commercially available (100)-oriented *p*-type Ge wafers with resistivity of 0.1–0.5 Ω cm. The substrates were cleaned in a 5% HF solution, followed by annealing at 350 °C for 10 min under a vacuum pressure (1.0×10^{-7} Pa). Subsequent plasma nitridation of the cleaned Ge surfaces was performed in the same chamber without exposure to air. Our plasma nitridation system, which can be operated under atmospheric pressure conditions, has a porous electrode to generate large-scale and high-density plasma.[6] The process chamber pressure was kept of the order of 10^3 Pa during plasma nitridation, and the other treatment conditions were as follows: nitrogen flow rate of 1.5 SLM (SLM denotes liters per minute at STP), rf power of 50 W, distance between the electrode and Ge substrate of 1 cm, and substrate temperature of 350 °C. The composition and chemical bonds of the nitrided surfaces were characterized by XPS using monochromated Al $K\alpha$ lines. The surface and cross-sectional structures of the as-nitrided layer and the layer after air exposure were investigated by transmission electron microscopy (TEM) and atomic force microscopy (AFM). In this study, we focused on humidity-dependent stability of the Ge_3N_4 layers. For this purpose, we exposed the nitride surfaces to the air at room temperature within our class 1 clean room under the controlled humidity of 40% or 80% and examined the transformation of the chemical bonds and surface morphology by XPS and AFM, respectively.

Figure 1(a) shows the Ge 3*d* spectrum obtained from the nitrided Ge surface after minimal air exposure of 40% hu-

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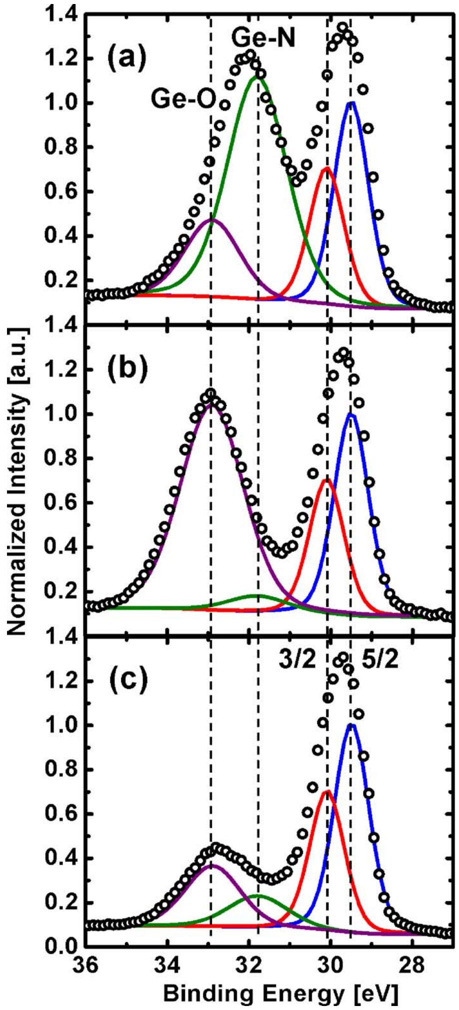

FIG. 1. (Color online) Results from peak fitting of normalized Ge 3*d* spectra; (a) was taken from the as-nitrided Ge(100) surface by high-density nitrogen plasma at 350 °C; (b) and (c) were taken after air exposure under 80% humidity condition for 12 h and 1 week, respectively. Chemical shift peaks at higher binding energy can be fitted well with two components by assuming chemical shift of 2.3 eV for Ge–N bonds and 3.4 eV for Ge–O bonds.

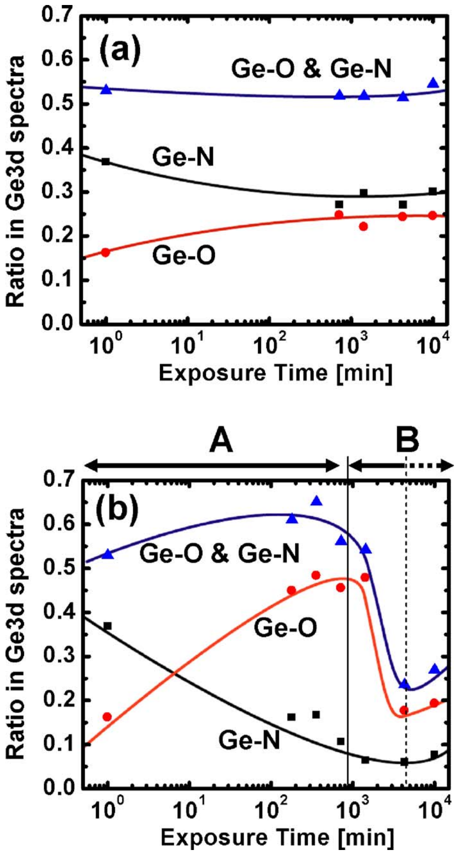

FIG. 2. (Color online) Change in the chemical shift components of the Ge 3*d* spectrum of nitrided Ge(100) surfaces during air exposure. Normalized intensities from Ge–N and Ge–O components, as well as total chemical shift intensity, were plotted as a function of the air-exposure time under (a) 40% and (b) 80% humidity conditions at room temperature. At region A, conversion of the Ge–N bonds to the Ge–O bonds is dominant, whereas drastic decrease in Ge–O component was observed at region B.

midity within a few minutes. The chemical shift component at higher binding energy can be fitted well with two components originating from Ge–N and Ge–O bonds, which are, respectively, shifted 2.3 and 3.4 eV from the bulk peak.[3,7] It is clear that the Ge–N bond is dominant on the initial (as-nitrided) surface. Angle-resolved XPS also revealed that most of the Ge–O bonds, that is, Ge oxide exists near the surface (data not shown). This is consistent with our previous report showing that, when we annealed the nitrided Ge surface at 500 °C under vacuum, the oxide layer selectively decomposed from the surface.[4] TEM observation showed that the thickness of the amorphous nitride was 3.5 nm and that the interface with the Ge substrates was abrupt at the atomic level (data not shown). In addition, the nitride surface was found from AFM observation to be smooth with a root mean square (rms) roughness of 0.17 nm [see Fig. 3(a)].

To understand the chemical reactions occurring on the surface of the Ge_3N_4 layer, the changes in the Ge 3*d* signal was recorded as the air-exposure time. Figure 2(a) summarizes the intensity changes of the total chemical shift components Ge–O and Ge–N and of the components from the Ge–N and Ge–O bonds under the lower humidity (40%). We found that, after the initial rapid oxidation, the following oxidation of the Ge_3N_4 layer proceeds gradually. Considering that the total intensity from the chemical shift components was almost constant during air exposure, we excluded the possibility of additional oxidation at the Ge_3N_4/Ge interface. Therefore, we can conclude that, in contrast to the rapid oxidation of the uppermost surface, the conversion of the Ge–N bonds within the nitrided layer to the Ge–O bonds is a rate-limited reaction. Since pure Ge_3N_4 layers have been reported to be highly resistant against oxygen diffusion,[8] it would appear that the initial rapid oxidation of the Ge_3N_4 is probably an effect of the moisture in the air.

In order to figure out the degradation mechanism of the Ge_3N_4 layers, we examined transformation of the nitride layer exposed to the higher-humidity air. The changes in the Ge 3*d* spectra when the Ge_3N_4 surface was exposed to the air with 80% for 12 h and 1 week are, respectively, shown in Figs. 1(b) and 1(c). Note that, although there was no significant change in the total intensity from the chemical shift component, most of the Ge–N bonds converted to Ge–O bonds after being exposed to air with 80% humidity for 12 h [Fig. 1(b)]. Then, the chemical shift peak from the Ge–O bonds also decreased largely after further air exposure for 1 week [Fig. 1(c)]. Figure 2(b) summarizes the degradation phenomena of the Ge_3N_4 layer caused by moisture in the air. In contrast to what was seen under the 40%-humidity condition [Fig. 2(a)], oxidation of the whole Ge_3N_4 layer proceeds in region A, followed by area B where the total chemical shift component shrinks, as also shown in Fig. 1(c). These

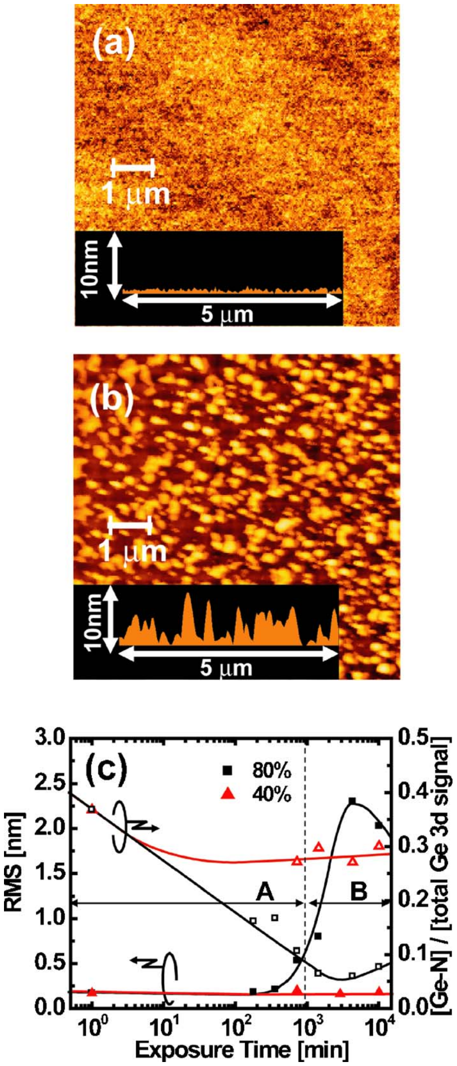

FIG. 3. (Color online) Change in surface morphology of the nitrided Ge(100) surfaces under different humidity conditions. (a) and (b) show AFM images of the nitrided surface after minimal air exposure and for 2 days in the clean room under 80% humidity, respectively. (c) Summary of the changes in root mean square roughness and normalized nitrogen content depending on the humidity conditions. Regions A and B labeled in Fig. 2(b) were also indicated.

results imply that the reactive hydroxyl groups in the air attack the surface of the Ge_3N_4 layers and transform Ge nitride into Ge oxide. Moreover, after the conversion, remarkable decrease in the chemical shift component at region B suggests structural change in the Ge surface.

The change in the surface morphology of the Ge_3N_4 layers during air exposure was next characterized by using AFM. Figures 3(a) and 3(b), respectively, show AFM images of Ge_3N_4 surfaces exposed to air with 80% humidity for about 1 min and for 2 days. It is clear that shorter air exposure does not affect the surface morphology of the Ge_3N_4 layer (rms: 0.17 nm) but longer exposure increased the surface roughness drastically. After exposure to air with 80% humidity for 1 week, the peak-to-valley (P-V) value eventually reached 10 nm. This P-V value was apparently larger than the initial thickness of the Ge_3N_4 layer. The changes in surface roughness of the Ge_3N_4 layers exposed to 40% and 80% humidity for 1 week are compared in Fig. 3(c) with the corresponding changes in nitrogen content (i.e., the changes in the ratio of the intensity of the chemical shift due to Ge–N bonds to the intensity of the total Ge 3d signal). Note that, at region A, in which conversion of Ge–N bonds into Ge–O bonds was the dominant reaction, the nitride surface remained smooth under both humidity conditions. Under the higher-humidity condition, however, surface roughness increased after this conversion was completed (region B). Under the lower-humidity condition, in contrast, the bond conversion proceeded gradually and the Ge_3N_4 surface remained smooth. We also observed quite similar humidity-dependent degradation of the Ge_3N_4 layers prepared by a different plasma nitridation technique using an electron-cyclotron-resonance plasma source. Therefore, these findings mentioned above were proved to be intrinsic to Ge_3N_4 films.

Given these results, we propose the following degradation model for Ge_3N_4 layers. Although the Ge_3N_4 layer is thermally stable in a vacuum and nitrogen ambient, moisture in the air has a great impact on the stability Ge_3N_4 layers. Since, in high humidity condition, there are much more hydroxyl groups, the nitride surface was oxidized. During this initial degradation, addition interface oxidation can be neglected and conversion of the nitride to the oxide proceeds while remaining a smooth surface during air exposure. After the bond conversion (oxidation), surface condensation of the Ge oxide forms oxide islands to cause surface roughness only for high-humidity conditions. The details of the atomistic reactions between hydroxyl groups and Ge_3N_4 surfaces and island formation mechanism are under investigation, but we can understand the reason for the contradictions in the stability of the Ge_3N_4 layers and for the oxygen incorporation into the nitride during fabrication and postannealing processes.

In summary, we systematically investigated the stability against air exposure of the Ge_3N_4 layers. We found that the hydroxyl groups attack and oxidize the nitride surface. In the degradation process, the surface roughness increases drastically after the Ge–N bonds are converted to Ge–O bonds. While the Ge_3N_4 layers directly formed on Ge substrate by plasma nitridation are very important and promising material in terms of the application for the passivation layers and the interfacial layers to fabricate high-k gate stacks on Ge substrates, these results regarding instability against moisture show that it is essential to take the best care of the moisture in the Ge-based device fabrication processes.

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