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Study on Hydrogen-based Reactive Ion Etching of Ovonic Threshold Switch (OTS) Materials for Phase Change Memory Devices

D. S. Kim[a], Y. J. Gill[a], Y. J. Jang[a], Y. E. Kim[a], and G. Y. Yeom[a,b]

[a] School of Advanced Materials Science and Engineering, SungKyunKwan University, 2066 Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 16491, Republic of Korea

[b] SKKU Advanced Institute of Nano Technology (SAINT), SungKyunKwan University, 2066 Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 16491, Republic of Korea

Ovonic threshold switch (OTS) materials are used in selector devices for phase change random access memory (PcRAM) circuits and are generally composed of chalcogenide compounds. In this study, etch characteristics of OTS material composed of Ge-As-Te have been investigated using reactive ion etching (RIE) by hydrogen-based gases such as H_2, CH_4, NH_3, etc. Among the investigated hydrogen-based plasmas, NH_3 showed the highest etch rate due to the high vapor pressures of the hydrides, but the formation of nitride compounds and the increased roughness were observed on the OTS surface. In the case of CH_4+NH_3 (1:1 ratio) plasma, the OTS material could be etched at high OTS etch rates without the formation of nitrogen compounds and without increasing the chemical and physical damage on the OTS surface through the formation of volatile CN-related compounds.

Recently, phase change random access memory (PcRAM) device has been intensively investigated as one of the most industrially applicable memory devices due to the excellent performance such as non-volatility, scalability, high speed, and low power consumption (1, 2). In general, when a current or voltage is applied to a lower electrode to a PcRAM, the phase of the phase change material changes from a crystalline to an amorphous state by Joule heating, and information is recorded by the differences in resistance (3, 4). The PcRAM device is operated through a cross-array structure, and an unintended leakage current occurs during operation. To solve this problem, an ovonic threshold switch (OTS) selector device is used in each cell of the PcRAM(5, 6). OTS materials are generally composed of chalcogenide compounds, and the combination of Ge-As-Te is generally used. The OTS selector layer is generally fabricated by etching using halogen gases. However, during the etching process, halides are formed on the sidewall of etched chalcogenide compounds, and which penetrate into the sidewalls of the OTS pattern and damage the phase change characteristics (7-10). Therefore, it is necessary to develop a dry etch process that reduces chemical damage to OTS materials and enables precise etching. In this study, an OTS material composed of Ge-As-Te was etched with various hydrogen based gases such as H_2, CH_4, NH_3, CH_4+H_2, and CH_4+NH_3. The chemical species generated in the plasma using these hydrogen based gases were identified through optical analysis and the etching characteristics of OTS materials using those gases were compared and, and the degree of etch damage was evaluated through the surface analysis after etching the OTS materials.

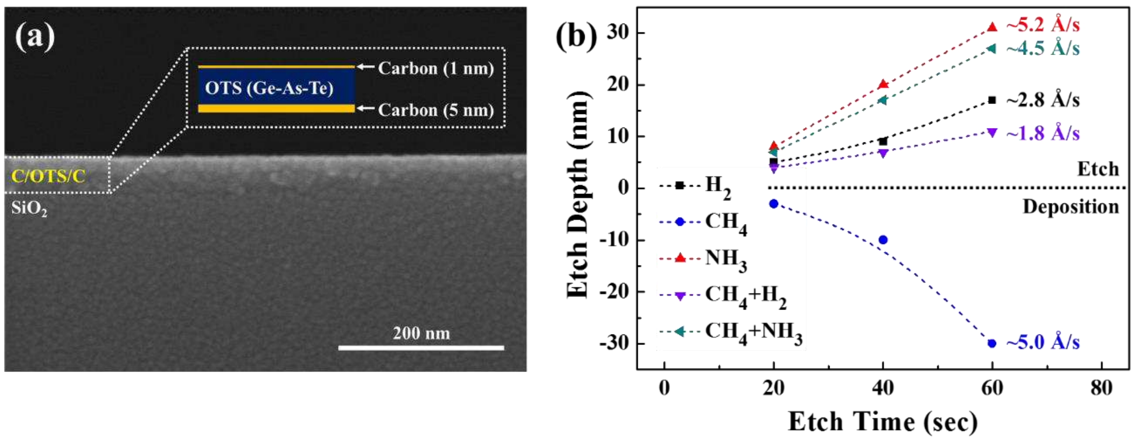

Figure 1. (a) Cross-sectional images of the multilayer thin film including the OTS layer stacked as C/OTS/C to prevent oxidation of OTS on SiO_2 substrate. (b) Etch depth of OTS layer as a function of etch time for hydrogen-based gases by inductively coupled plasma-reactive ion etcher (ICP-RIE).

Figure 1(a) shows the field emission scanning electron microscopy (FE-SEM) image of the 31 nm thick multilayer C/OTS/C thin films stacked as carbon (1 nm)/OTS (25 nm)/carbon (5 nm) to prevent oxidation of OTS on SiO_2 substrate. Figure 1(b) shows the etch depth of OTS materials measured as a function of etch time using 300 W of the 13.56 MHz inductively coupled plasma (ICP) source power and 50 W of 12.56 MHz bias power (a little lower rf frequency to prevent the power interference) with 5 mTorr of hydrogen gases such as H_2, CH_4, NH_3, CH_4+H_2 (1:1 ratio), and CH_4+NH_3 (1:1 ratio). The OTS etch rates by H_2, CH_4+H_2, NH_3, and CH_4+NH_3 were 2.8, 1.8, 5.2, and 4.5 Å/s, respectively; while no etching of OTS was observed for CH_4. In the case of CH_4 plasma, hydrocarbon was deposited on the surface instead of etching, and the highest etch rate was observed with NH_3 plasma. In general, the OTS materials can forms hydrides such as GeH_4, AsH_3, and TeH_2, and their boiling points are -88.5, -62.5, and -2.2 °C, respectively (the standard enthalpy of formation (ΔH_f^0) at 298.15 °K for GeH_4, AsH_3, and TeH_2 are 90.8, 66.4 and 99.7 kJ/mol, respectively). Therefore, when hydrogen based plasma such as H_2, NH_3, CH_4+H_2, CH_4+NH_3 is used, the OTS material can be easily etched by forming a hydrogen based volatile compounds. (In the case of the CH_4 plasma, even though hydrogen atoms dissociated from the CH_4 plasma can also form volatile compounds with OTS materials, due to the carbon remaining on the surface, instead of etching, a hydrocarbon polymer appeared to be deposited on the OTS surface.) Also, the binding energies of H-H, H-C, H-N are 436, 413, and 391 kJ/mol, respectively; therefore, it is expected that more hydrogen atoms are dissociated for NH_3 than other gases investigated. The highest OTS etch rate with NH_3 plasma shown in Figure 1(b) among the hydrogen based gases investigated could be related to the highest hydrogen atom concentration in the plasma.

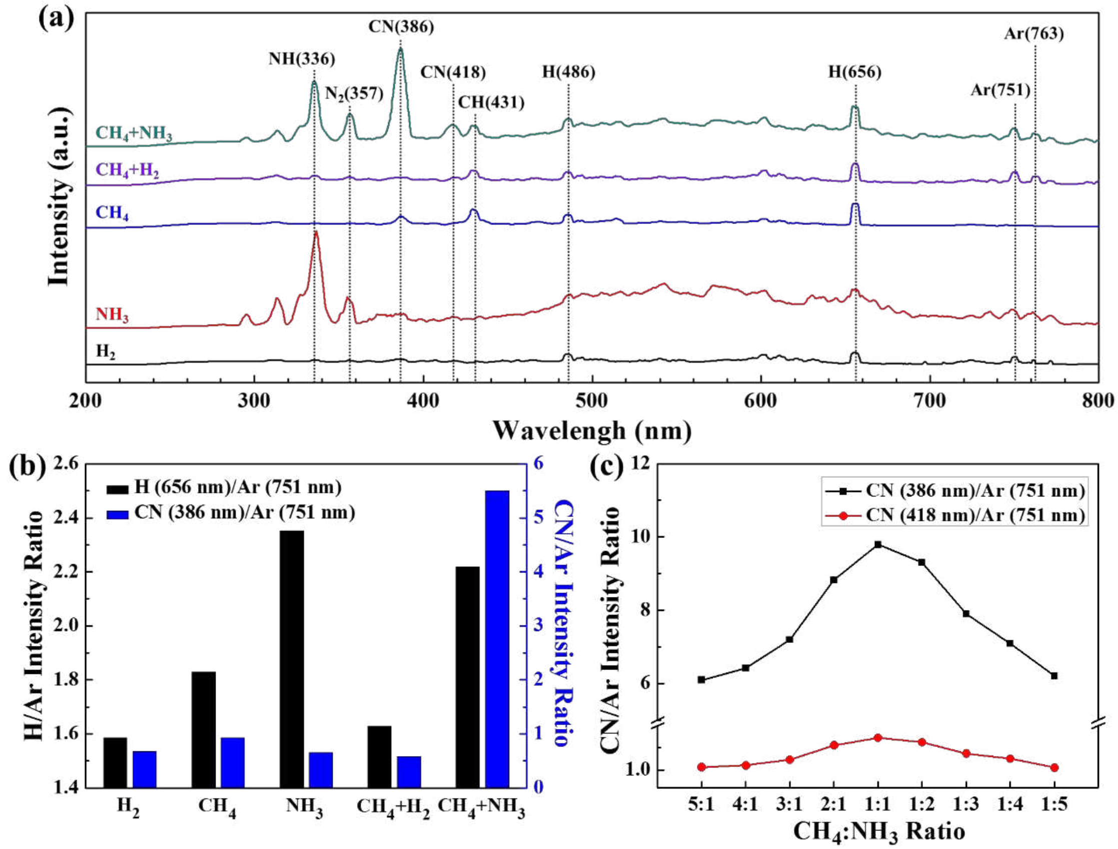

Figure 2. (a) OES spectra for hydrogen-based plasmas such as H_2, NH_3, CH_4, CH_4+H_2 (1:1), and CH_4+NH_3 (1:1). Small amount of Ar was added to the gases for the estimation of the hydrogen concentration in the plasma. (b) The optical intensity ratios of H (656 nm)/Ar (751 nm) and CN (386 nm)/Ar (751 nm) for (a). (c) The optical intensity of CN/Ar according to the ratio of CH_4 and NH_3.

Using optical emission spectroscopy (OES), the amount of hydrogen atoms in the hydrogen-based plasma was investigated, and the results are shown in Figure 2(a). The process conditions are the same as in Figure 1, but for comparison of optical intensities, Ar was added and the ratios of optical intensity to that of Ar were compared. The OES emission peaks related to H atoms such as H_β and H_α were identified at 486 and 656 nm in addition to Ar peaks at 751 and 763 nm. To estimate the relative hydrogen atom concentration dissociated in the plasma, the optical peak intensity ratio of H (656 nm)/Ar (751 nm) was taken, and the results are shown in Figure 2(b). The highest H/Ar ratio was observed for NH_3 among hydrogen based plasmas investigated, possible indicating the highest etch rate of OTS with NH_3. However, although the etch rate is the highest with NH_3, nitride can be formed on the OTS surface by nitrogen generated in NH_3 plasma, and carbide can be formed in CH_4 plasma. Therefore, it is necessary to remove nitrogen and carbon generated from NH_3 and CH_4 plasmas during the process not to form nitride or carbide on the OTS surface. In the CH_4+NH_3 plasma, unlike other plasmas, it can be seen that the CN peak increases significantly in OES. In the case of CN, volatile carbon nitrides are formed (The boiling point of cyanogen, C_2N_2, is -21.1 °C and that of HCN is 25.6 °C. The $\Delta H_f^{\,0}$ at 298.15 °K required to form cyanide is ~67.2 kJ/mol, and the $\Delta H_f^{\,0}$ of HCN and C_2N_2 are 135.1 and 309.1 kJ/mol, respectively. Therefore, it can be expected that HCN will be mainly formed compared to C_2N_2, which is slightly higher than the hydride formation energy for OTS materials). In order to compare the ratio of CN generated in CH_4+NH_3 plasma, the ratio of CH_4:NH_3 was adjusted and the differences in optical intensity were observed as shown in Figure 2(c). When the ratios of CN (386 nm)/Ar(751 nm) and CN (418 nm)/Ar(751 nm) were observed, it was confirmed that the CN concentration was the highest at the 1:1 ratio of CH_4:NH_3.

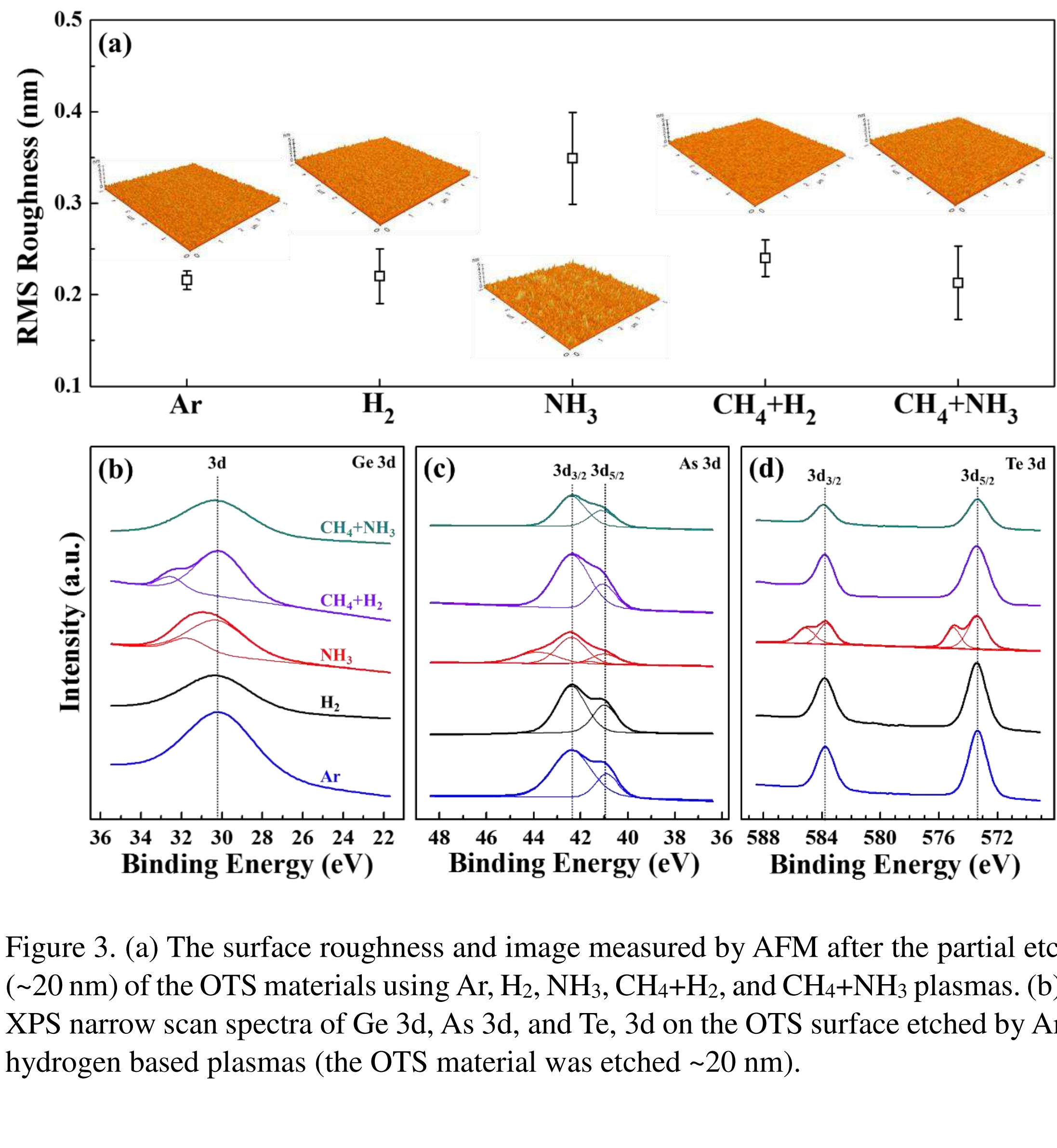

Figure 3. (a) The surface roughness and image measured by AFM after the partial etching (~20 nm) of the OTS materials using Ar, H_2, NH_3, CH_4+H_2, and CH_4+NH_3 plasmas. (b)~(d) XPS narrow scan spectra of Ge 3d, As 3d, and Te, 3d on the OTS surface etched by Ar and hydrogen based plasmas (the OTS material was etched ~20 nm).

After etching of OTS materials using hydrogen-based plasmas (the OTS was etched ~20 nm in depth), the surface RMS roughness of the OTS was measured by atomic force microscopy (AFM), and the results is shown in Figure 3(a). In the case of the Ar sputtering of the OTS material, surface roughness was ~0.21 nm and was similar to that of OTS etched by H_2 plasma (~0.22 nm). The surface roughness etched by NH_3 plasma, even though the etch rate was the highest among the hydrogen-based plasmas, the surface roughness was the highest as ~0.35 nm. It can be expected that nitrogen generated in the NH_3 plasma formed a nitride on the OTS surface, which has low volatility and thus increased surface roughness (the boiling point of a Ge nitride such as Ge_3N_4 is 900 °C, and the other component nitrides such as $Te_{3-4}N_4$ and AsN are not well known). When OTS was etched with CH_4+H_2 and CH_4+NH_3 plasma, the surface roughness was the second highest with CH_4+H_2 while that with CH_4+NH_3 was also similar to those of Ar and H_2 possibly due to the formation of carbide on OTS surface for CH_4+H_2 while no nitride or carbide is formed with CH_4+NH_3. To investigate the chemical contamination of etched OTS surface by the etching hydrogen-based plasmas, the binding states of Ge 3d, As 3d, and Te 3d were investigated. After the etching with H_2 and CH_4+NH_3, the 3d peaks of Ge at 30.2 eV, $3d_{5/2}/3d_{3/2}$ peaks of As at 40.9/42.4 eV, and $3d_{5/2}/3d_{3/2}$ peaks of Te at 573.4/583.8 eV, which are similar to those of the OTS surface etched by Ar sputtering were observed indicating no changes in the chemical binding states of the OTS material after etching by H_2 and CH_4+NH_3. However, in the case of the etching by NH_3 plasma, for 3d Ge peak, an additional Ge peak at 31.8 eV, which is related to Ge-N could be clearly observed. Also, for 3d As and 3d Te peaks, additional high binding energy peaks were observed, respectively, indicating the formation of arsenic nitride and tellurium nitride. Therefore, it can be seen that CH_4+NH_3 plasma appears to be suitable for rapid etching while minimizing physical and chemical damage to OTS materials.

Acknowledgments

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