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Investigation of plasma species, etch products and surface modification during etching of Ge, Sb and Se-based materials in CH₄-H₂-Ar plasmas

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Abstract Organometallic positive ions were identified in inductively coupled plasmas by means of mass spectrometry during the etching of Ge-Sb-Se materials in CH₄-H₂-Ar mixtures. Observation of polymetallic species (M_x-R, M = Ge, Sb, Se, x > 2, R = H_y or CH_z) points out that recombination reactions occur in the plasma. Correlation with x-ray photoelectron analysis, showing the presence of C-M moieties indicates that chemical etching processes take place.

Keywords: plasma etching, mass spectrometry, Ge-Sb-Se etch products, XPS.

1. Introduction

The general aim of this study is to obtain information on the etching mechanisms of the Ge-Sb-Se ternary material in methane-based plasmas. Up to now Ge-Sb-Se chalcogenide has been patterned quite exclusively in halogen-based plasma. Methane-based plasma chemistry has proven to be successful for the etching of III-V and II-VI semiconductors, while the study of Ge-Sb-Se etching in such chemistry is non-existent, hindering the development of such plasma processes. The critical prerequisite is to obtain basic information during and after the etching of the stoichiometric GeSe₂ and Sb₂Se₃ materials, as well as from the elementary Ge, Sb and Se. Here we focus on the identification of hydride and organometallic ion species as obtained by mass spectrometry analysis of the plasma and on the characterisation of the sample surface using quasi *in situ* x-ray photoelectron spectroscopy.

2. Experimental and methods

Studies are carried out using an inductively coupled plasma reactor described elsewhere [1]. Study is performed first in H₂-Ar mixture and then upon adding a few % CH₄ (from 4 to 8) to the mixture. Typical plasma process conditions are 700 W excitation power, 5 mTorr pressure, 75 to 130 sccm total gas flow rate, -150 to -200 V substrate self bias, 0 to 8% CH₄ in H₂-Ar, which ratio varied from 1 to 1.5.

Optical emission spectroscopy (OES – Horiba iHR550 + Synapse CCD) operates in the range 200-900 nm. Mass spectrometry (MS – Hiden Analytical EQP1000) is carried out on the positive ions in the range 1-300 amu. The nose of the spectrometer is fitted with a 100µm in diameter orifice and located at 15 cm from the centre of the plasma chamber and 2 cm above the sample holder. To provide information on the plasma chemistry and etch products both techniques require long plasma runs and thus bulk samples, which either were bought as wafer (Ge), ingot (Sb) or pellet (Se), or synthesised as deposition targets (GeSe₂, Sb₂Se₃, Ge_{19.5}Sb_{17.8}Se_{62.7}) [2].

Vacuum transfer from the plasma reactor to the X-ray photoelectron spectroscopy chamber (XPS – Specs XR50M x-ray source, Focus500 monochromator, Phoibos

HR150 electron analyser) requires the use of thin (< 1 mm) samples; these were prepared as films (Sb, Sb₂Se₃, Ge₃₉Se₆₁, Ge₁₉Sb₂₁Se₆₀) deposited onto a Si substrate from the preceding bulk materials. Spectra were acquired with a pass energy of 14 eV and an energy step of 0.1 eV. An electron flood gun was used to compensate for electrical charging effects. CasaXPS software [3] is used for data processing, considering a Shirley model [4] for the inelastic background and LF lineshapes [5] for curve fitting.

3. Plasma diagnostics

Comparison of the OES measurements carried out in CH₄-H₂-Ar plasma without and with a Ge-Sb-Se target evidences the presence of Sb and Ge atoms in the plasma uniquely in the presence of the target, *i.e.* when etching the material. However, no emission from Se atoms is noticed, opposite to what is observed when etching in SF₆ plasma [6].

A multi linear regression (MLR) method is used to analyse the MS measurements. MLR is applied to extract the contribution of each ion within a cluster by solving:

$$S = \alpha * I + e \quad (1)$$

The vector S is the experimental data delimited in a defined mass range; the vector α contains all the regression coefficients; the matrix I contains the isotopic distribution of each ion potentially involved in S ; and e represents the residual. Within a M_xC_yH_z⁺ cluster, the lighter ion ($z = 0$) and the heaviest ion ($z = z_{\max}$) delimit the number of ions contained in the matrix I by taking into account all ions from $z = 0$ to $z = z_{\max}$. Starting from the theoretical abundance pattern of M_xC_y⁺, the isotopic distribution is shifted according to the number of H bonded. The purpose is to predict a spectrum S_p using the same matrix I with the estimated vector α_p as represented in:

$$S_p = \alpha_p * I + e_p \quad (2)$$

The vector α_p is estimated from α such as the sum of the squared residuals $\sum(e - e_p)^2$ is minimized. An example illustrating the method is given in Fig. 1 below.

In the case of an H₂-Ar plasma, the MLR analysis shows unambiguously that the dominant ions are GeH₃⁺ and Ge⁺; Sb⁺ and SbH⁺; SeH₂⁺ and Se⁺, respectively for elemental Ge, Sb and Se samples and in the 70-79, 121-126 and 74-85 amu m/z ranges.

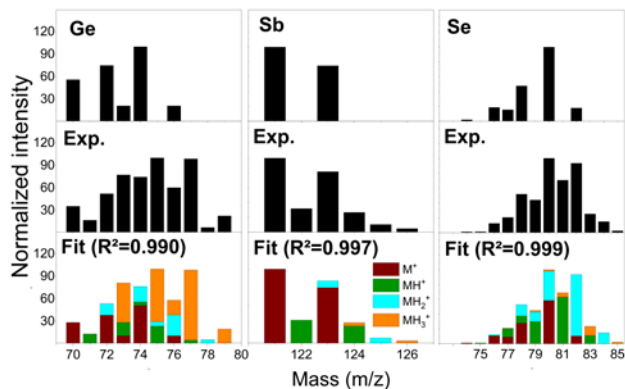


Fig. 1. Illustration of the MLR method. Top: natural isotopic distribution of Ge, Sb, Se. Middle: ion mass spectra recorded during the etching in H₂-Ar (50-50) at 6mTorr, 700W, -200V bias, 130sccm. Bottom: predicted spectra using the MLR analysis and resulting contributions.

Therefore, and as expected from thermochemistry data, chemical etching most likely provides GeH₄ and SeH₂, while sputtering processes release Ge and Sb. Binary ions are also observed: Ge₂H₃⁺, Ge₂H₄⁺ and Ge₂H₅⁺ (m/z = 140 to 156 amu); Sb₂⁺ and Sb₂H⁺ (m/z = 242 to 248 amu); Se₂⁺, Se₂H⁺ and Se₂H₂⁺ (m/z = 152 to 164 amu). This indicates that recombination processes occur in the gas phase.

When operating in CH₄-H₂-Ar mixture, organometallic ions are observed in addition to the previous species. As an example Figure 2 presents MS signal observed for the SbCH_x (m/z = 133 to 140 amu), SbC₂H_x (m/z = 147 to 154 amu) and SbC₃H_x (m/z = 160 to 168 amu) during the etching of Sb. MRL analysis (Fig. 3) indicates that dominant ions in these three groups are respectively SbCH₃⁺, HSbCH₃⁺ and H₂SbCH₃⁺; Sb(CH₃)₂⁺ and HSb(CH₃)₂⁺; Sb(CH₃)₃⁺. Let us point out that it is not clear whether these dominant ions originate from the ionisation, eventually dissociative, of methyl-Sb, dimethyl-Sb and trimethyl-Sb molecules or from the recombination between Sb and CH_x radicals.

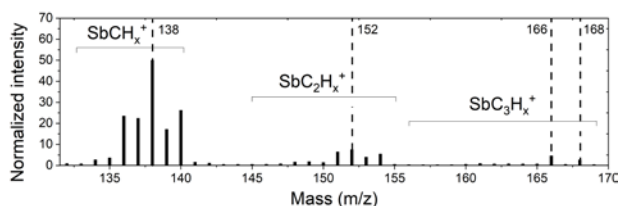


Fig. 2. Ion mass spectrum recorded during the etching of Sb in CH₄-H₂-Ar (8-55-37) at 5mTorr, 700W, -200V, 95sccm.

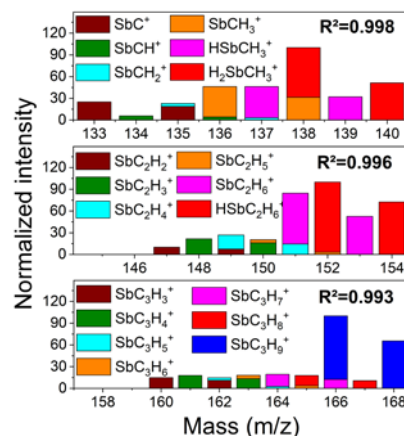


Fig. 3. MLR analysis of the Sb-organometallic ions MS signal presented in Fig. 2.

Similarly the MS data during etching of Se shows the potential presence of SeCH_x⁺ and SeC₂H_x⁺ ions, in the m/z = 90 to 114 amu region, and of Se₂CH_x⁺ ions in the m/z = 171 to 175 amu region. MLR analysis was able to support the existence of such species, with dominant contributions respectively for SeCH₃⁺, HSeCH₃⁺ and H₂SeCH₃⁺; Se₂CH₃⁺ and H₂Se₂CH₃⁺. Concerning Ge, MS signals potentially corresponding to GeCH_x⁺ and GeC₂H_x⁺ ions are observed (m/z = 85 to 106 amu region), yet MLR analysis was not successful in reason of the overlapping with C_xH_y⁺ species.

Etching of GeSe₂, Sb₂Se₃, Ge_{19.5}Sb_{17.8}Se_{62.7} materials in CH₄-H₂-Ar plasma generates a considerable number of signals (Fig. 4). For Sb₂Se₃ and Ge_{19.5}Sb_{17.8}Se_{62.7}, the large cluster from m/z = 195 to 222 amu suggests the presence of mixed SeSbC_xH_y⁺ species; the MLR analysis supports this and gives the SeSb⁺, SeSbH⁺ (m/z = 195 to 206 amu) and SeSbC⁺, SeSbCH⁺ (m/z = 214 to 220 amu) as the dominant ions.

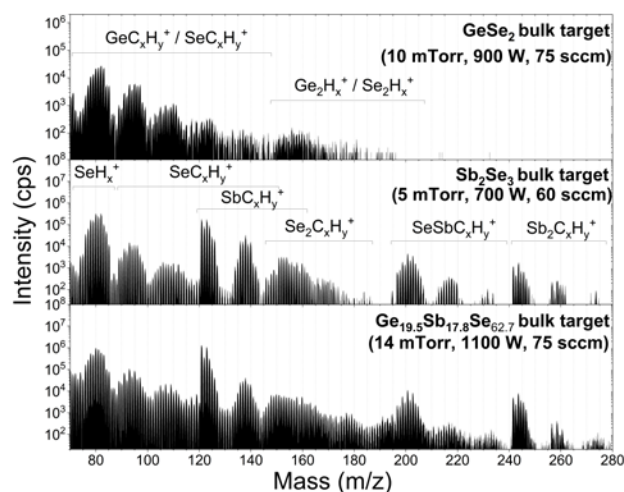


Fig. 4. Ion mass spectra recorded during the etching of GeSe₂, Sb₂Se₃ and Ge_{19.5}Sb_{17.8}Se_{62.7} materials in CH₄-H₂-Ar (8-55-37).

For GeSe₂ the only groups detected are the Ge_xC_xH_z⁺ and Se_xC_yH_z⁺ ones identified previously. But, comparing the GeSe₂ and Ge-Sb-Se MS data, it may be possible that the group between m/z = 190 to 196 in the case of the Ge-Sb-Se compound relates to mixed GeSbH_x⁺ ions.

4. Surface analysis

Fig. 5 below presents an example of the surface modification observed by XPS after etching in CH₄-H₂-Ar plasma. For Sb (Fig. 5a) and Ge (Fig. 5b), components ascribed to (M)-M-C_x species are observed in addition to the elemental M-M component. For the binary materials, the surface oxide ((Se)-M-O components in Fig.5c-d) is eliminated and new components are present. For the Ge₃₉Se₆₁ sample (Fig. 5f), the components at 30.7 and 31.5 eV are attributed to (Ge)-Ge-(C,Se)₃ and to Ge-(C,Se)₄ species. In agreement, analysis of the Se 3d core level (not shown) presents two new features at 55.2 and 55.6 eV that can be ascribed to (C)-Se-Ge and (C)-Se-C environments respectively. For the Sb₂Se₃ sample (Fig. 5e), the contributions at 32.9 and 33.8 eV are ascribed to (Se)-Sb-(C,Se)_x (x= 1, 2). The Se 3d core level (not shown) presents also new features at 54.4 and 55.3 eV respectively attributed to (C)-Se-Sb and (C)-Se-C environments. For both materials, it is difficult to distinguish the [MSe_x] original motif from the (Se)-M-C_x since carbon and selenium have identical electronegativity values (2.55); however these components present a larger width than the [MSe_x]; in addition the bonding of a methyl group instead of a carbon atom could induce the slight shift observed. These two arguments plead in favour of the (Se)-M-C_x interpretation.

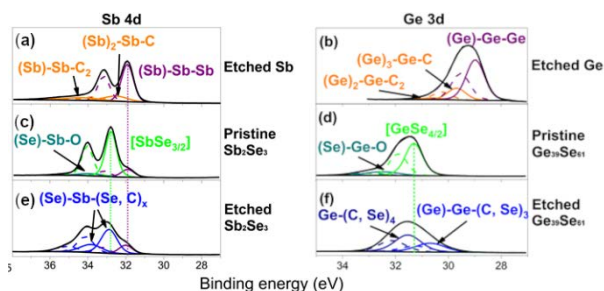


Fig. 5. Sb 4d and Ge 3d core level spectra. After etching Sb (a), Ge (b), Sb₂Se₃ (e), Ge₃₉Se₆₁ (f) materials in CH₄-H₂-Ar (4-58-38) plasma 3mTorr, 700W, -150V bias, 75sccm. (c) and (d) present the binary compounds before etching.

5. Conclusion

Using mass spectrometry, detection of M-hydride and M-organic ions (M = Ge, Sb, Se) in the H₂-Ar and CH₄-H₂-Ar plasma phase was observed during etching of Ge, Sb, Se, GeSe₂, Sb₂Se₃ and Ge-Sb-Se compounds. Multilinear regression analysis supports the formation of M_xH_y⁺ and M_xC_yH_z⁺ species and SbSeC_xH_y⁺ mixed compounds. Yet, although these ions unambiguously relate to the release of some M-containing products from the material surface, no conclusion can be drawn concerning the nature of the

original neutral etch products; moreover, the observation of poly-M ions clearly puts forward the existence of recombination processes in the gas phase. Observation of the C-M moieties at the compound surface by XPS after etching in CH₄-H₂-Ar plasma indicates a modification of the surface chemistry resulting from adsorption of -CH_x reactive species. As a general conclusion, the combination of plasma diagnostics and surface analysis proves that etching of these materials is achievable in methane-based plasma chemistry and operates *via* the formation of hydrocarbon-based etch products.

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