Investigation of plasma species, etch products and surface modification during etching of Ge, Sb and Se-based materials in CH_4-H_2-Ar plasmas

T. Meyer[1], A. Girard[1], M. Bouska[2], P. Němec[2], V. Nazabal[3] and C. Cardinaud[1]

[1] *Université de Nantes, CNRS, Institut des matériaux de Nantes Jean Rouxel, Nantes, France*
[2] *Department of Graphic Arts and Photophysics, University of Pardubice, Pardubice, Czech Republic*
[3]*Université de Rennes, CNRS, Institut des Sciences Chimiques de Rennes, Rennes, France*

Abstract Organometallic positive ions were identified in inductively coupled plasmas by means of mass spectrometry during the etching of Ge-Sb-Se materials in CH_4-H_2-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 $GeSe_2$ and Sb_2Se_3 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 H_2-Ar mixture and then upon adding a few % CH_4 (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% CH_4 in H_2-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 ($GeSe_2$, Sb_2Se_3, $Ge_{19.5}Sb_{17.8}Se_{62.7}$) [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, Sb_2Se_3, $Ge_{39}Se_{61}$, $Ge_{19}Sb_{21}Se_{60}$) 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 CH_4-H_2-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 SF_6 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:

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

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:

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

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

In the case of an H_2-Ar plasma, the MLR analysis shows unambiguously that the dominant ions are $GeH_3^+$and Ge^+; Sb^+ and SbH^+; SeH_2^+ and Se^+, respectively for elemental Ge, Sb and Se samples and in the 70-79, 121-126 and 74-85 amu m/z ranges.

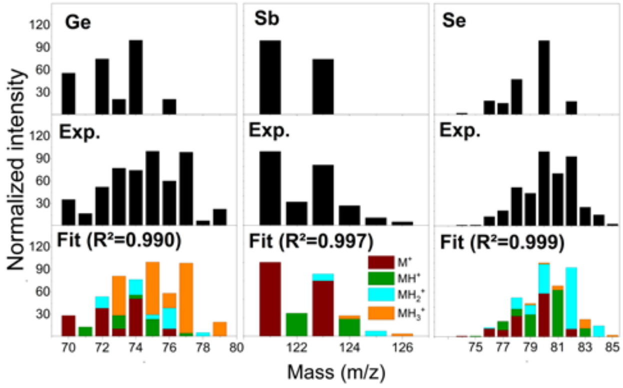

Fig. 1. Illustration of the MLR method. Top: natural isotopic distribution of Ge, Sb, Se. Middle: ion mass spectra recorded during the etching in H_2-Ar (50-50) at 6mTorr, 700W, -200V bias, 130sccm. Bottom: predicted spectra using the MLR analysis and resulting contributions.

Therefore, and as expected from thermochemistry data, chemical etching most likely provides GeH_4 and SeH_2, while sputtering processes release Ge and Sb. Binary ions are also observed: $Ge_2H_3^+$, $Ge_2H_4^+$ and $Ge_2H_5^+$ (m/z = 140 to 156 amu); Sb_2^+ and Sb_2H^+ (m/z = 242 to 248 amu); Se_2^+, Se_2H^+ and $Se_2H_2^+$ (m/z = 152 to 164 amu). This indicates that recombination processes occur in the gas phase.

When operating in CH_4-H_2-Ar mixture, organometallic ions are observed in addition to the previous species. As an exemple Figure 2 presents MS signal observed for the $SbCH_x$ (m/z = 133 to 140 amu), SbC_2H_x (m/z = 147 to 154 amu) and SbC_3H_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 $SbCH_3^+$, $HSbCH_3^+$ and $H_2SbCH_3^+$; $Sb(CH_3)_2^+$ and $HSb(CH_3)_2^+$; $Sb(CH_3)_3^+$. 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.

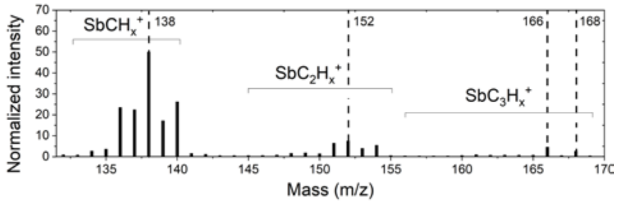

Fig. 2. Ion mass spectrum recorded during the etching of Sb in CH_4-H_2-Ar (8-55-37) at 5mTorr, 700W, -200V, 95sccm.

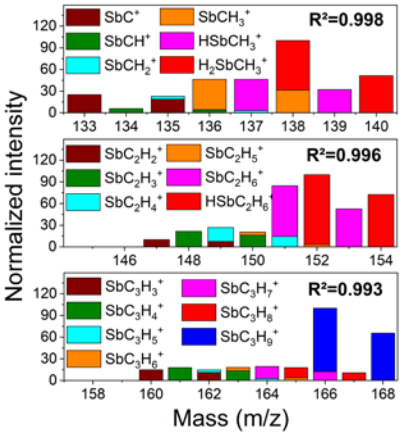

Fig. 3. MLR analysis of the Sb-organometallic ions MS signal presented in Fig. 2.

Similarly the MS data during etching of Se shows the potential presence of $SeCH_x^+$ and $SeC_2H_x^+$ ions, in the m/z = 90 to 114 amu region, and of $Se_2CH_x^+$ 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 $SeCH_3^+$, $HSeCH_3^+$ and $H_2SeCH_3^+$; $Se_2CH_3^+$ and $H_2Se_2CH_3^+$. Concerning Ge, MS signals potentially corresponding to $GeCH_x^+$ and $GeC_2H_x^+$ 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 $GeSe_2$, Sb_2Se_3, $Ge_{19.5}Sb_{17.8}Se_{62.7}$ materials in CH_4-H_2-Ar plasma generates a considerable number of signals (Fig. 4). For Sb_2Se_3 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.

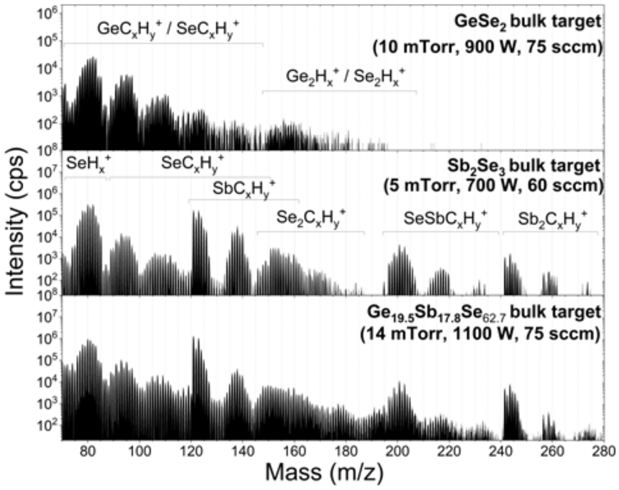

Fig. 4. Ion mass spectra recorded during the etching of $GeSe_2$, Sb_2Se_3 and $Ge_{19.5}Sb_{17.8}Se_{62.7}$ materials in CH_4-H_2-Ar (8-55-37).

For $GeSe_2$ the only groups detected are the $Ge_xC_xH_z^+$ and $Se_xC_yH_z^+$ ones identified previously. But, comparing the $GeSe_2$ 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 CH_4-H_2-Ar plasma. For Sb (Fig. 5a) and Ge (Fig. 5b), components ascribed to (M)-M-Cx 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 $Ge_{39}Se_{61}$ 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 Sb_2Se_3 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.

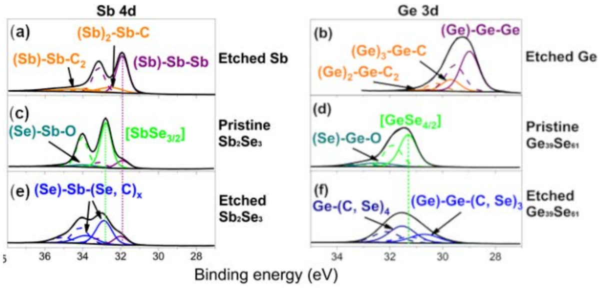

Fig. 5. Sb 4d and Ge 3d core level spectra. After etching Sb (a), Ge (b), Sb_2Se_3 (e), $Ge_{39}Se_{61}$ (f) materials in CH_4-H_2-Ar (4-58-38) plasma 3mTorr, 700W, -150V bias, 75sccm. (c) and (d) present the binary compounds before etching.

5. Conclusion

Using mass spectrometry, detection of M-hydride and M-organic ions (M = Ge, Sb, Se) in the H_2-Ar and CH_4-H_2-Ar plasma phase was observed during etching of Ge, Sb, Se, $GeSe_2$, Sb_2Se_3 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 CH_4-H_2-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.

6. References

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