



Product study in the interaction of selected metal and semiconductor surfaces with H₂ plasma generated species

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Introduction

Plasmas can be utilized to initialize chemical and physical processes through the interaction between plasma constituents and solid/gaseous matter, resulting in a multitude of subsequent reaction pathways.

The reactivity of excited H-atoms towards tin and in general towards elements of the 14th group of the periodic table is known in the literature for decades, as well as the thermodynamic instability of the resulting metal hydride species. The catalytic effect of metal surfaces on the homolytic covalent bond cleavage is also known since long. The nature of the involved heterogeneous chemistry and the deeper understanding of the corresponding processes gained substantial interest regarding high-energy hydrogen plasmas in the presence of metals.

The initial interaction in the formation of metal hydrides is a heterogeneous gas/surface reaction of excited atomic H and metal atoms, whereby successively H-M bonds are formed. The volatile metal hydrides thus formed subsequently desorb and may adsorb on other (metal) surfaces and decompose again, which may represent a contamination.

Experimental setup

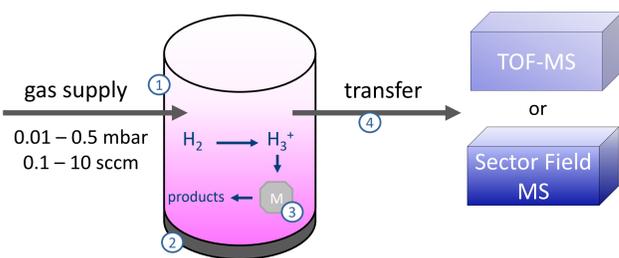


Fig. 1: Schematic and simplified mechanism of metal hydride formation. Ionic species are identified directly by the TOF-MS. Neutral products are detected using post-ionization via EI with the sector field MS.

A custom low-pressure RF discharge generates the reagent ions H₃⁺ within a hydrogen plasma fed by an adjustable continuous gas flow (1). The RF generator (2) provides the energy to sustain the discharge, which is classified as a high-density plasma [1]. Typical operation pressures range between 0.01 and 0.5 mbar, which is compatible with the conditions in the different stages of the coupled mass spectrometers.

The continuously generated ions interact in the plasma area with the metal samples (3) and the neutral/ionic reaction products enter the MS via viscous transport (4).

Methods

- Mass spectrometer:
- C-TOF time of flight mass spectrometer with custom ion transfer stage (Tofwerk AG, Thun, Switzerland)
 - MAT95XP double-focusing sector field mass spectrometer with EI source (Thermo Fisher Scientific, Waltham, MA, USA)
- RF-power supplies:
- RFG-13-100 13.56 MHz RF generator with 100 W output power (Barthel HF Technik, Aachen, Germany)
 - 40.68 MHz MatchingCube i-300 with 300 W (Barthel HF-Technik, Aachen, Deutschland)
- Gases:
- Hydrogen 5.0 and Argon 5.0 (Messer Group GmbH, Krefeld, Germany)
- Software:
- Gaussian 16. [2] and GaussView 6.0.16

Basic chemical behavior and thermodynamic stabilities

The RF plasma primarily generated electronically excited H species and H⁺ ions. The latter react with molecular hydrogen to form H₃⁺. In contrast to H₂, the adsorption of reactive H species on tin surfaces leads to subsequent formation of volatile stannane (SnH₄), which either decomposes on the surface or desorbs into the gas phase [3,4].

Tin oxide is reduced by atomic hydrogen to tin metal and water. In the gas phase, a reaction cascade leads to a multitude of various tin hydrides. In this scheme (Eley-Rideal mechanism), more H is consumed than expected by a simple recombination of adsorbed and newly penetrating H atoms.

Stannane tends to spontaneously decompose into the elements, a process, which is accelerated by reactive surfaces (1st order kinetics [2]) upon forming tin islands via layer growth.

Fig. 2 shows schematically the reaction channels of these tin compounds [3].

The thermodynamic instability of the various neutral and ionic tin hydrides and their spontaneous dissociation into the elements is experimentally well known. Ab initio calculations support this hypothesis. The species are shown in Fig. 3. Ab initio calculations for SnH₂⁺ and SnH₄⁺ did not lead to any stable structures – this is also experimentally verified.

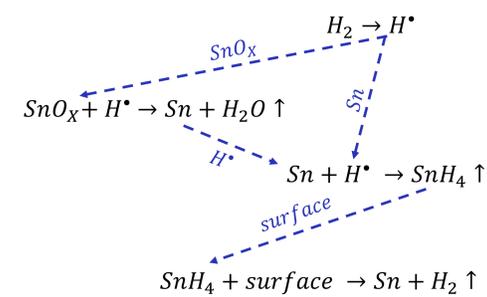


Fig. 2: Schematic representation of the different coupled reaction channels.

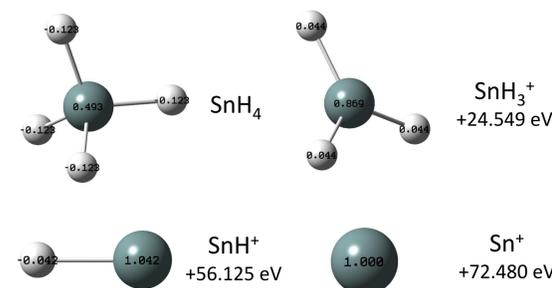


Fig. 3: Optimized structures of tin hydrides labeled with the Mulliken charges. The energies are relative to neutral stannane.

Experimental results

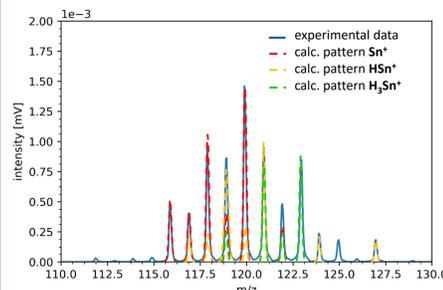


Fig. 4: Mass spectrum of plasma generated tin hydrides and calculated isotopic patterns.

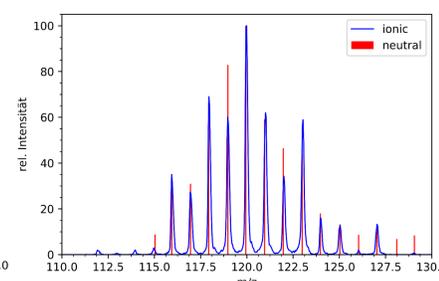


Fig. 5: Superimposed mass spectra of ionic and post-ionized "neutral" tin hydrides.

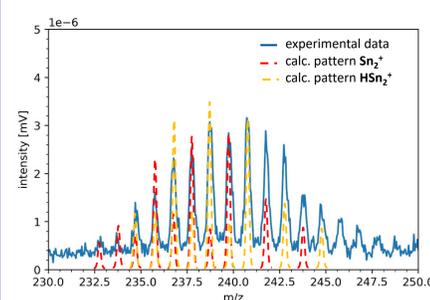


Fig. 6: Mass spectrum of plasma generated dimeric tin hydrides and calculated isotopic patterns.

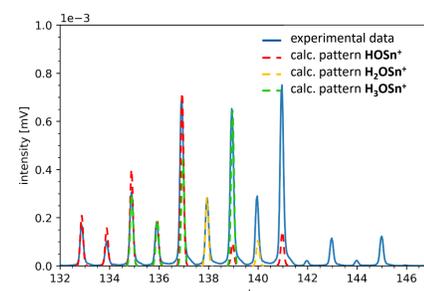


Fig. 7: Mass spectra of plasma generated oxygenated tin hydrides and calculated isotopic patterns.

In the mass spectra, natively ionic and post-ionized "neutral" tin hydrides as well as oxygenated tin compounds were detected. The comparison of the recorded mass spectrum with calculated isotopic pattern [5] reveals the distinct patterns of various ionic tin hydrides of the type SnH_x⁺, especially SnH⁺ and SnH₃⁺. SnH₂⁺ and SnH₄⁺ were not detected due to the thermodynamic instability (cf. Fig. 4). The rich isotopic pattern of Sn is fully reproduced and thus used for compound identification.

The accordance of both mass spectra (cf. Fig. 5) suggest a common neutral stannane (SnH₄) molecule as precursor, since only neutrals can pass the potential barrier of +5 kV for the EI ion source of the sector field MS.

To a lesser extent, oxygenated tin hydrogen compounds of the type OSnH_x⁺ are present in the plasma effluent as well (cf. Fig. 7). The oxygen source is either an oxide layer present on the metal surface or residual gas phase oxygen.

Conclusion / Outlook

Conclusion

- It is confirmed that plasma generated excited hydrogen species generate volatile metal compounds via hydride formation upon interaction with the metal surface.
- Ab initio calculations show the decreasing stability of the ionic tin hydrides as compared to the initial SnH₄.
- Ionic SnH₂⁺ and SnH₄⁺ appear to be extremely unstable
- Experiments with other metals such as nickel and tantalum reveal no signals of the corresponding ions, most probably due a strong protective oxide layer, very low stability of the ionic hydrides or insufficient sensitivity of the employed set-up.

- The very good agreement of the mass spectra obtained with the two different instruments strongly suggest an initial neutral stannane molecule as precursor, which is to some extent ionized through the plasma species.

Outlook

- Images of metal surfaces with SEM before and after treatment with H-plasma and their generated species and layer growth mechanism of tin islands.
- Further ab-initio calculations regarding the stability of metal hydrides and simulations of the formation of hydrides on metal surfaces with MD simulations.

Literature

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Acknowledgement

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