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Ion bombardment induced segregation effects in VD_x studied by SIMS and SNMS

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Abstract

Secondary ion mass spectrometry (SIMS) and complementary secondary neutral (particle) mass spectrometry (SNMS) investigations on VD_x samples were carried out to study deuterium segregation effects induced by ion bombardment. It could be shown that the sputter process causes a distortion of the near-surface region, which leads, due to the extremely high mobility of deuterium in vanadium, to a deuterium segregation to the surface, i.e. a deuterium enrichment in the sputtered area, and at the same time to a deuterium impoverishment in the bulk (secondary preferential sputtering effect).

Keywords: Vanadium–deuterium; SIMS; SNMS; Segregation; Preferential sputtering

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1. Introduction

By bombarding the surface of solids with low-energy (a few keV) heavy ions, such as Ar^+, target atoms are sputtered from the topmost monolayers of the solid. Sputtered species are emitted as neutrals to a major part, or as ions, both positive and negative, as atomic or as cluster particles. Their relative abundance provides a direct measure of the composition of the layer that has been removed. Analysis of the sputtered species is the most sensitive of the surface analysis techniques with an information depth (cf. Fig. 1) of about 1 nm. The most commonly used sputtering technique is the direct collection and analysis of the sputtered ionized species (secondary ions) by mass spectrometry (SIMS). However, the secondary ion yield of a species strongly depends on its chemical environment in the solid (matrix effect). Due to the presence of either electropositive (e.g. sodium) or electronegative (e.g. oxygen) ions at the target surface the secondary ion yields can vary by orders of magnitude by enhancing the ionisation probability (e.g. oxygen induction effect). The strong influence of the matrix on the ion yields impedes an accurate determination of relative concentrations.

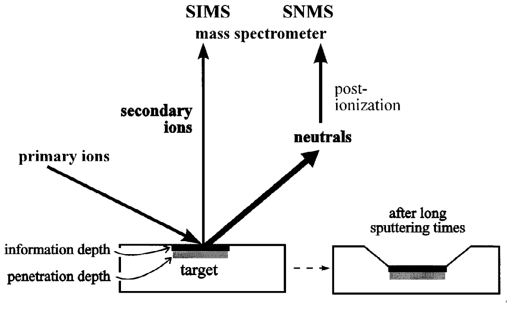

Fig. 1. Principle of SIMS and SNMS.

Matrix effects can largely be avoided when the sputtered neutral particles are used for composition analysis (SNMS). The mass analysis still requires ions for detection, however, in SNMS the sputtering and ionization processes are decoupled by postionizing the sputtered neutrals after emission from the sample surface. SNMS is more quantitative than SIMS since the matrix effect is negligible. However, cluster ions are observable only to a minor extent compared to SIMS, so chemical information gets lost.

The sputtering process involves complex collision cascades with a series of angular deflections and energy transfers between many atoms in the surface layer of the solid up to the penetration depth (a few nm) of the incident primary ion (cf. Fig. 1). This unavoidably leads to a more or less displacement of the lattice atoms from their equilibrium positions, i.e. to a distortion or disordering of the structure in a thin surface layer. This structure is different from that of the unaffected material, but is still

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crystalline. The chemical composition in this layer remains nearly constant as long as fast segregation processes can be excluded. Under these conditions an analysis of the sputtered material reflects the composition of the surface and of the bulk, apart from the problems caused by matrix effects. If multicomponent samples are ion bombarded, different sputtering coefficients of the components can result in a preferential removal of the component with the highest sputtering coefficient. When analysing again the sputter-removed particles this effect can normally not be observed, the composition of the sputtered particles corresponds to that of the bulk, the composition of the remaining surface, however, has changed in such a sense that the component with the smaller sputter rate is enriched compared to the bulk concentration. The situation can change if highly mobile components are present (see below).

In order to use SIMS or SNMS to determine depth profiles it is necessary to remove controlled thicknesses of the surface layer and to follow specific signals (secondary ion intensities). At constant current densities the sputter time is a measure for the sample depth. In depth profile measurements the distortion zone migrates with constant thickness into the interior of the sample to the same extent as material is removed from the outer surface.

A strong feature of SIMS and SNMS is the ability to detect hydrogen and its isotopes directly over a wide range of concentrations. Therefore, these techniques are extremely attractive to study metal–hydrogen systems. The use of these techniques provides information about the kinetics and catalysis of hydrogen uptake [1], the influence of surface impurities on these processes [2] and on hydrogen solubility and permeation [3], and about structural and electronic effects [4]. In this paper the main emphasis is only on the investigation of deuterium[1] segregation to the surface of vanadium targets loaded with deuterium using SIMS and especially SNMS, whereby mass spectra as well as depth profiles are discussed.

2. Experimental

The SIMS- and SNMS-equipments are described in detail in [5]. SIMS measurements were carried out using a commercial SIMS setup (Balzers, quadrupole mass-analyzer QMG 511) with primary ions (Ar^+) of 3 keV energy and a beam current density of 1×10^{-6} A cm^{-2}, corresponding to a removal of about 10 nm h^{-1}. The base pressure in the UHV chamber was below 2×10^{-8} Pa; during the measurements an Ar pressure of about 2×10^{-3} Pa was established.

The SNMS spectra were measured by an INA 3 (Specs). During the measurements an argon plasma was established for direct ion bombardment, but also for the postionization process. The applied bombardment energy of about 600 eV corresponds to an erosion rate of about 1 nm s^{-1}.

The vanadium foils (Heraeus GmbH; thickness: 40 μm; purity: 99.99%) were charged with different amounts of deuterium (highest purity; from a TiFe–D reservoir) in an external UHV chamber at different temperatures up to the compositions $VD_{0.03}$, $VD_{0.15}$ and $VD_{0.26}$. Thin foils have been chosen in order to allow a complete depth profile throughout the entire thickness.

3. Results and discussion

The SIMS spectra from the VD_x foils show qualitatively analogous secondary ion emission patterns to those obtained in former investigations on cylindrical samples (see [5]).

The main results obtained from the SIMS spectra, one of them is shown in Fig. 2a (after removal of the contamination layer), are:

- The purity of the base material is high, as the total secondary ion yields are very small (small influence of

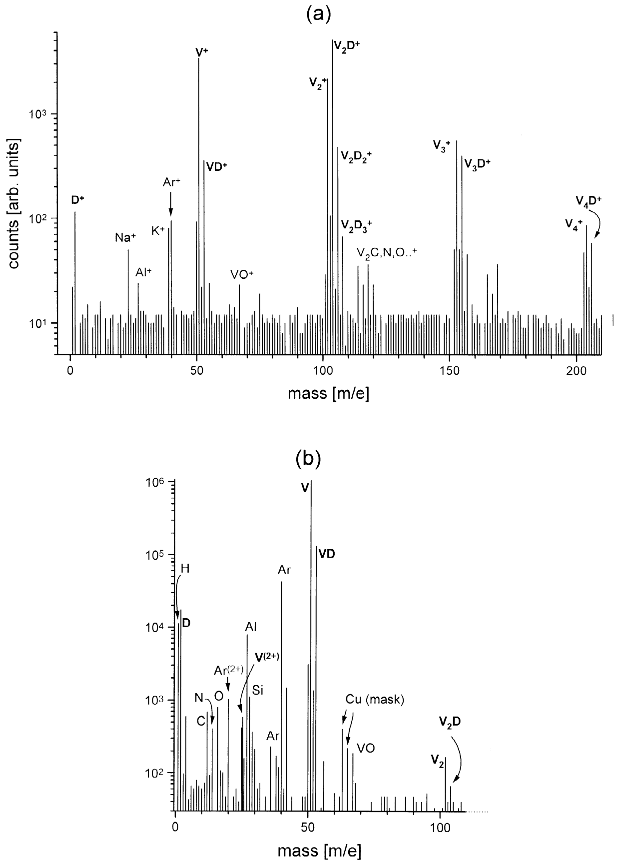

Fig. 2. Positive (a) SIMS, and (b) SNMS spectra of a $VD_{0.15}$ foil.

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[1] Deuterium which is normally absent in the residual gas of the analysing chamber is used instead of hydrogen in order to be able to distinguish clearly between influences of hydrogen (H) from the atmosphere and the hydrogen (D) within the vanadium samples [3].

the oxygen induction effect). Even elements such as Na, K or Al, which typically occur with high intensities because of their high ionization probability, are obtained only with small intensities.

- The total yield of directly emitted positive ions increases with increasing D content (hydrogen induction effect) [5].
- The ratio of D to V signals is nearly identical for samples with different D contents in the bulk, but is even high for the sample with the smallest D concentration ($x=0.03$). The ratio begins to decrease only at bulk concentrations smaller than $x=0.01$.

Fig. 2b shows the SNMS spectrum of a deuterium-charged vanadium sample in a depth of approx. 1500 nm. As is typical for SNMS (and in contrary to SIMS), due at least to the postionization of emitted neutrals, no higher cluster ions than V_2^+ can be found. Besides the signals of Cu (from the sample holder and mask) and Ar (plasma gas) impurity elements such as Al and Si in vanadium can be clearly identified. The small signals of C, O and (minor) N indicate a relatively low residual contamination of the material. The presence of D in the sample is reflected by the signals of D, VD, VD_2 and V_2D. For all three VD_x samples, the ratios for V and D (cluster-)signals are independent of the deuterium content x, as has been found with SIMS. In addition, the deuterium-specific sputter yields are high, even at smallest D content. Thus, the SNMS spectra completely confirm the results obtained by SIMS. Deuterium is enriched in the near-surface region which is directly analyzed. The nearly constant intensity of D specific signals, independent of the bulk concentration, indicates that the observed behaviour cannot be attributed to a normal preferential sputtering of deuterium involving a fast segregation to the surface. If such an effect was true, the D signals should be nearly proportional to the D concentration in the bulk. This means that the deuterium solubility of the surface region is affected and determined by the ion bombardment. The disordered structure of the surface layer induces the segregation of the highly mobile deuterium. A steady state or a new phase is spontaneously established by fast diffusion from the interior of the foil to the surface. In this case a depth profile should show a loss of deuterium in the remaining bulk material after removal of several layers of the deuterium-enriched phase. To prove this, the signals of the secondary neutrals V and V_2, D and VD and O and C were followed for several hours during ion bombardment, keeping the sputtering rate constant (Fig. 3).

Since matrix effects can largely be neglected in SNMS, in contrast to SIMS, the changes in the signal for one species can be attributed to a change in concentration. The time axis is a measure for the sample depth (1 s≡1 nm). In the depth profile we can distinguish four regions (marked (1)–(4) in Fig. 3).

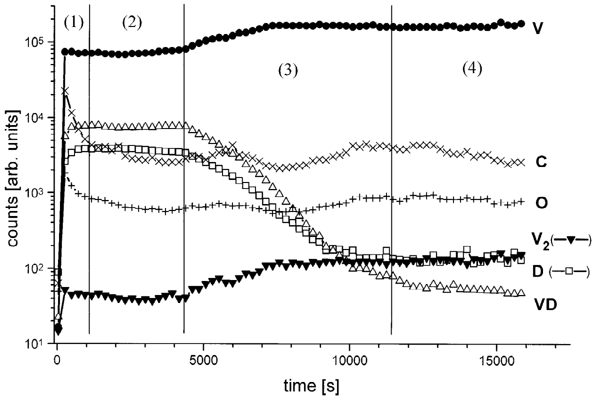

Fig. 3. Long-term SNMS measurement on a $VD_{0.15}$ foil.

Phase (1) can be interpreted as a contamination layer. The signals for O and C decrease rapidly with increasing sample depth. Simultaneously, the D signals (D and VD) increase, i.e. the deuterium solubility increases with decreasing O and C content. In region (2), all signals remain nearly constant, the deuterium-specific ones at a high concentration level. In the third region (3), the D specific signals decrease, the pure V signals increase, both of them reaching a level of a deuterium-free V foil (region (4) after approximately 11 500 s).

The thickness of the contamination layer (region (1)) depends on the D content; it increases with decreasing D content, i.e. with a decreasing D activity during the loading process. The most interesting result is the decrease of the D and VD intensities in region (3) indicating that the deuterium concentration in the bulk, and, thereby, the deuterium supply from the bulk to the surface, is no longer sufficient for establishing the steady state in the distorted surface region regarding the deuterium content. This explanation is confirmed by the fact that the region of constant deuterium contents (region (2)) is smaller for foils with lower D contents. The total effect of D impoverishment in the remaining sample can be understood as a secondary preferential sputtering effect: Due to the ion-bombardment process the lattice in the near-surface region becomes distorted in such a way that the deuterium solubility is enhanced. Deuterium, therefore, segregates out of the bulk to the surface and the deuterium-enriched new surface phase is removed by sputtering. The increase of the pure V specific and also the total sputter yields is not fully understood at this time.

Exact absolute compositions of the surface layer are not yet obtainable due to the lack of suitable reference material which allows a determination of relative sensitivity factors for D and V. Assuming that all the sputter-removed D derives from the volume beneath the sputter spot throughout the thickness of the foil, a rough estimation yields a composition according to the β-phase hydride V_2D. Such a composition could also be responsible for the fact that the V_2D^+ ion is the one with the highest emission intensity and detection sensitivity in SIMS spectra from VD_x samples.

Despite the fact that the sputter-induced segregation effect compromises the ability of SIMS and SNMS to study directly the bulk behaviour of metal hydrogen systems, both techniques are powerful tools, due to their high detection sensitivity for hydrogen and its isotopes and the emission of positive and negative cluster ions, for the study of the diverse interesting aspects of metal (alloys) hydrogen systems [6].

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