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Anomalous signal formation in secondary ion mass spectrometry of palladium

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Abstract

Cesium ions bombarding a high-purity palladium (Pd) target are shown to sputter out negative ions incompatible with stable isotopes of Pd. These unusual ions possess a mass of (Pd + 1), and they may possibly arise from the Pd–H reaction occurring in the ion-bombarded area. It is also shown that dimers of Pd are emitted exclusively as negative ions, with positive dimers virtually undetectable. The process whereby the dimer emission occurs in such a selective manner is still unclear. (Int J Mass Spectrom 189 (1999) 173–179) © 1999 Elsevier Science B.V.

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In secondary ion mass spectrometry (SIMS), which analyzes atomic and/or molecular ion species sputter ejected from a solid surface, the relative abundance of collected ions provides a direct measure of the chemical composition of the removed area. In the so-called static mode, the uppermost monolayers can be chemically analyzed [1,2]; this is unattainable by other surface analytical techniques, e.g. Auger electron spectroscopy and x-ray photoelectron spectroscopy. For dynamic SIMS, on the other hand, chemical information on the uppermost surface is less accurate because of the secondary effects of bombarding ions, typically atomic mixing [3].

The ion-formation process in SIMS is crucially affected by two factors: the ionization potential or electron affinity of ejected particles, and the surface work function [3]. The fluxes of positive and negative ions are formulated as

$$n^{+} = C \exp\left[(\varnothing - \mathrm{I})/K\right] \tag{1}$$

and

$$n^{-} = C' \exp\left[(A - \varnothing)/K'\right] \tag{2}$$

where I and A are the ionization potential and electron affinity of ejected particles, respectively, $\varnothing$ is the surface work function, and C, C', K, K' are constants [3].

In principle, negative ions, as well as positive ions, are emitted from monoatomic metals if the electron affinity is positive [4]. However, metal atoms are mostly electro-positive, possessing an electron affinity lower than the corresponding surface work func-

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tion. Secondary ions ejected from a contaminant-free, monoatomic metal surface are therefore predominantly positive provided the projectiles are chemically inert [cf. Eq. (2)]. Practical SIMS projectiles, however, are so chemically active that their interaction with the target gives rise to a significant change in surface work function. Cesium ions (Cs^+), for example, significantly lower the work function of the target surface to favor the emission of negative ions (see later). Indeed, Cs^+ ions bombarding a metal surface knock out positive and negative atomic ions in comparable abundance [5], in striking contrast to O^+, which exclusively generates positive ions.

Because of their stable isotopes, most elementary metals display two or more signals in their SIMS spectra. As a matter of course, the signal-intensity distribution in the mass spectra of positively and negatively charged atoms should be similar if they are emitted from the same area on an impurity-free monoatomic target. According to our recent investigation, this does not hold for palladium (Pd); positive and negative ions sputtered out by Cs^+ ions exhibit differing spectral structures. Specifically, the negative spectra involved intense hydride signals, regardless of an extremely low background pressure and a very high sample purity. We report here this anomalous signal formation, giving brief discussions on possible ion-formation processes.

The original sample material was a polycrystalline Pd sheet (99.99% purity) supplied by the New Hydrogen Energy (NHE) Laboratory. The sheet was cut into small pieces 5 × 5 mm in size, in order to serve as SIMS samples. Prior to mounting in the SIMS machine (ATOMIKA-4000), each sample was rinsed ultrasonically to remove nonvolatile surface contaminants. Some samples were preheated at 600 °C for outgassing, using an auxiliary ultrahigh vacuum (UHV) chamber, but no difference in mass-spectral structure was recognized between outgassed and nonoutgassed samples. In mass analysis, 8-keV Cs^+ ions were focused into a microbeam ~50 μm in diameter, with their total current regulated to ~100 nA. Our SIMS machine, which is equipped with an O^+ ion gun in addition to the Cs^+ one, covers the mass range of 1–250 u, and its base pressure is 2×10^{-8} Pa ($\sim 1.5 \times 10^{-10}$ Torr) or lower. The main residual gases inside the chamber were CO and H_2, as monitored with a quadrupole mass spectrometer. Unfortunately, an Ar^+-ion gun is not installed in our SIMS chamber, so precleaning of the sample surface was not possible. Because crystalline Pd interacts strongly with hydrogen, residual hydrogen was thought to affect the signal formation. To confirm this, high-purity (99.95%) deuterium gases were occasionally introduced into the SIMS chamber through a variable leak valve.

Fig. 1 shows typical SIMS spectra of Pd recorded for the same surface area in positive and negative modes. The respective signals in positive mode correspond to stable isotopes, with their relative intensity corresponding well to the relative abundance of the pertinent isotope [Fig. 1(a)]. The spectral structure in the negative mode was quite different; extra signals occupied the mass positions that were signal-free in the positive mode [Fig. 1(b)]. For other metals such as copper (Cu), molybdenum (Mo), and tungsten (W), positive and negative ions yielded identical spectra. Moreover, the mass region of Pd exhibited no signal for the non-Pd metals, and this ensures that the extra signals were not attributable to instrumental impurities released from ion–optical components. We may thus conclude that the unusual signal formation in the negative mode was intrinsic to Pd.

The extra signals might have their origin in bulk and/or surface impurities, but it is not likely that our Pd samples originally contained bulk impurities in amounts detectable by SIMS, because the as-received sample material was of very high purity. Another possibility is that some impurity was incorporated into the sample during the sample-preparation process. One way to ascertain this is to measure signal intensities as a function of sputtering time or depth. Fig. 2 shows the depth profiles for signals A (m/z 100), G ($^{106}Pd^-$), H (m/z 107), I ($^{108}Pd^-$), and J (m/z 109) in Fig. 1(b), among which signals A, H, and J were extra signals. Signal A rapidly weakened with increasing sputtering time, indicating that this signal originated in some surface impurity [6]. The intensities of signals G and I, which stemmed from stable ^{106}Pd and ^{108}Pd, lowered very slowly, whereas the intensities of

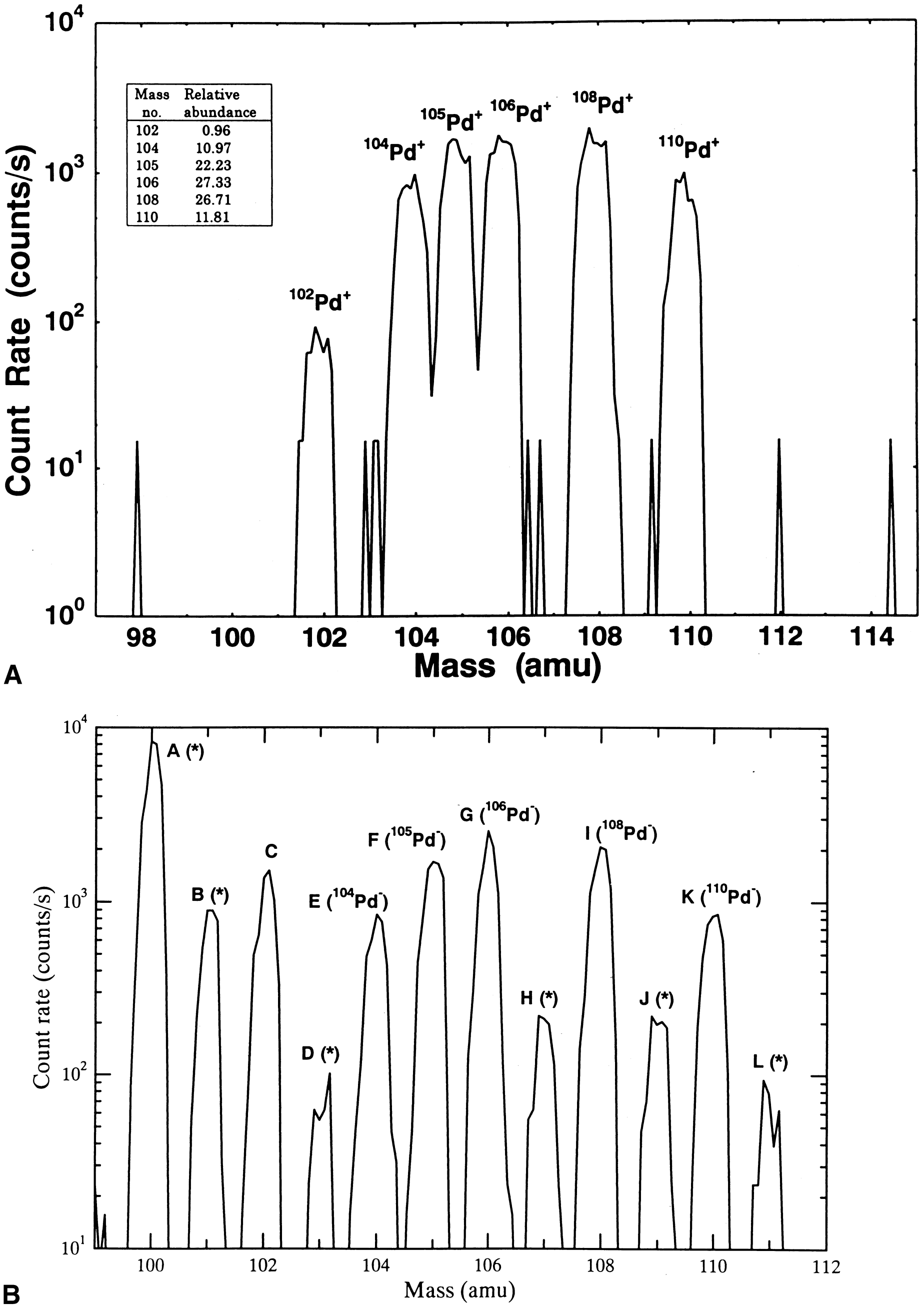

Fig. 1. Raw SIMS spectra of Pd for the same area on the same sample, recorded in the positive (a), and negative mode (b). Tabulated in (a) are the stable isotopes of Pd and their relative abundance. For clarity, the respective signals in (b) are denoted by the letters A through L. The asterisks indicate unidentified signals. Signal C at *m/z* 102 was caused by $^{102}\mathrm{Pd}^{-}$ and an unknown impurity.

signals H and J rose at a gentle gradient after an initial weakening, surpassing signals G and I after 10–14 minutes of sputtering. The latter type of depth profile is inexplicable in terms of surface impurities; signals J and H had no relation to impurities present on the original sample surface. Perhaps these signals were

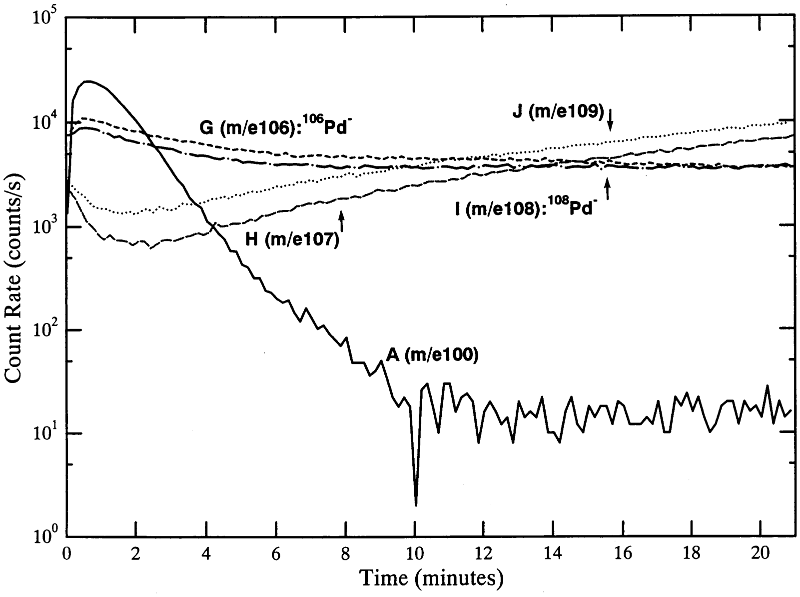

Fig. 2. Depth profiles for signals A, G, H, I, and J in Fig. 1(b). The incident ion beam was scanned during depth profiling, and the signals were detected from the central portion of the scanned area.

due to some chemical compound synthesized during ion bombardment.

Fig. 3 shows the negative-mode spectrum recorded just after the depth profiling in Fig. 2. Note that the signal-intensity distribution differs markedly from the original one in Fig. 1(b). For clarity, the qualitative

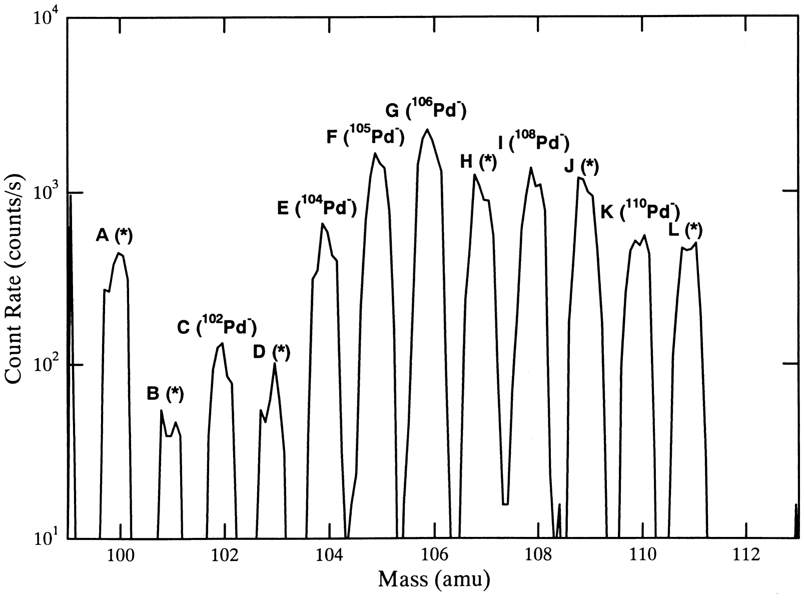

Fig. 3. Negative-mode spectrum recorded just after the depth profiling in Fig. 2. Ions emitted from the center of the crater formed in depth profiling were collected. The letters A through L correspond to the same letters in Fig. 1(b), respectively.

Table 1
Intensity change associated with depth profiling for the negative signals in Figs. 1(b) and 3

Symbol	*m/z*	Ion species	Intensity change
A	100	unknown	weakened
B	101	unknown	weakened
C	102	^{102}Pd + unknown	weakened
D	103	unknown	unchanged
E	104	^{104}Pd	unchanged
F	105	^{105}Pd	unchanged
G	106	^{106}Pd	unchanged
H	107	unknown	intensified
I	108	^{108}Pd	unchanged
J	109	unknown	intensified
K	110	^{110}Pd	unchanged
L	111	unknown	intensified

intensity change associated with depth profiling is presented in Table 1 for the respective signals. The unidentified signals, except for signal D at *m/z* 103, are roughly classified into two groups: weakened and intensified. Signal B at *m/z* 101, together with signal A (*m/z* 100), belongs in the former group, whereas signals H (*m/z* 107), J (*m/z* 109), and L (*m/z* 111) belong in the latter. Signal C at *m/z* 102 was caused by ^{102}Pd$^-$ and impurity ions, the latter being reduced to a negligible level by prolonged Cs$^+$ bombardment for depth profiling.

The mass positions of signals H, J, and L correspond to (^{106}Pd + 1), (^{108}Pd + 1), and (^{110}Pd + 1), respectively. In a simple interpretation, these signals might be due to PdH$^-$ ions formed through a Pd–H reaction. Palladium-hydrogen is the most typical of exothermic occlusion systems [7]. The process whereby Pd occludes hydrogen is the H diffusion into Pd. The diffusing H atoms eventually reside at the interstitial octahedral positions of the fcc Pd lattice to form the β Pd–H phase [8]. This process is generally physical, entailing no Pd–H bond formation except at extremely high hydrogen pressures of the GPa region [9]; occluded H atoms escape from Pd into the gas phase by reducing the ambient pressure. At a hydrogen pressure of 10^{-8} Pa, the [H]/[Pd] ratio in a Pd sample should be on the order of 10^{-3} [10], which is ostensibly too low to produce (Pd + 1) signals competing with the normal Pd signals in intensity (cf. Fig. 3). However, the above interpretation was proven to be reasonable by introducing deuterium gas into the SIMS chamber. In Fig. 4, for example, a signal corresponding to ^{110}PdD$^-$ is seen at *m/z* 112, verify-

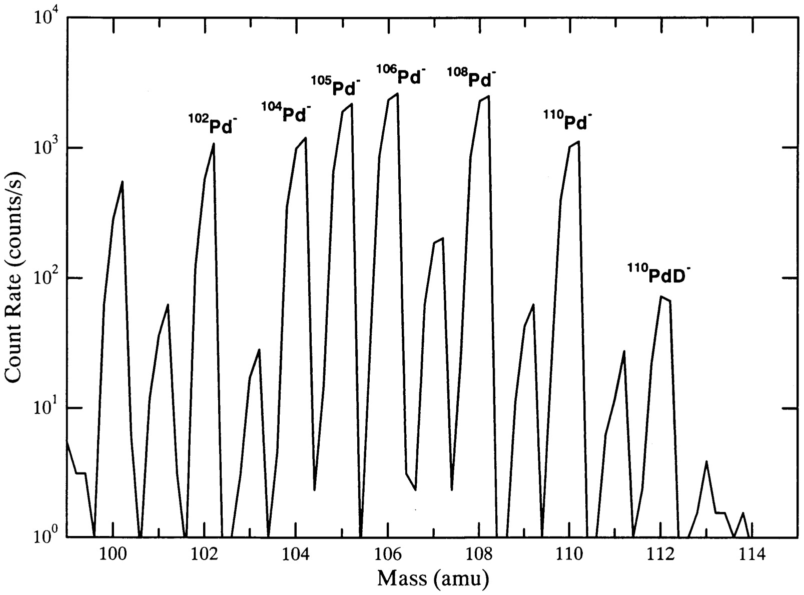

Fig. 4. SIMS spectrum of the Pd area recorded in a deuterium-gas ambience. The deuterium pressure was ~2 × 10^{-7} Pa, one order of magnitude higher than the background pressure.

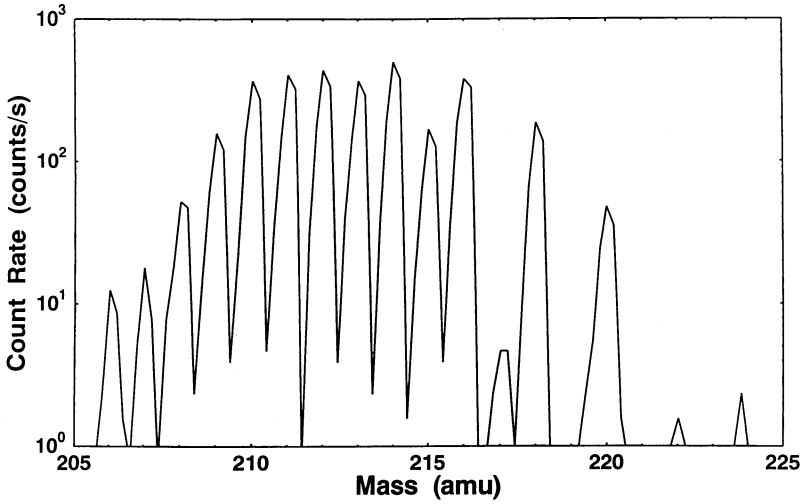

Fig. 5. Mass area of Pd dimers recorded in the negative mode. This mass area was signal free in the positive mode.

ing that the Pd–D bond formation actually took place at the Cs^+-bombarded area, regardless of a deuterium pressure as low as 2×10^{-7} Pa. Thus, we now come to the conclusion that residual hydrogen played a role in forming the extra signals H (*m/z* 107), J (*m/z* 109), and L (*m/z* 111) in Figs. 1(b) and 3.

From a chemical point of view, it is probable that H atoms adsorbed on Pd are negatively charged to form a weak chemical bond with surface Pd atoms. However, such a surface Pd–H bond will be broken by impacting Cs^+ ions, and therefore it is unlikely that the H^- adsorption led to the sputter ejection of abundant PdH^- ions as described here under a UHV condition. We suspect that the emission of intense PdH^- ions arose from the interaction of Pd with occluded hydrogen under Cs^+ bombardment.

By field-emission scanning electron microscopy, microscopic "pyramids" were found to grow on the Pd surfaces exposed to Cs^+ ions (data not shown). It is widely accepted that ion-induced atomic surface diffusion underlies the growth of such pyramids and related surface features [11,12]. Also, the sputtering ion beam has the effect of mixing surface and subsurface layers [3]. This atomic mixing should have been appreciable in our case because the primary ion current density amounted to $\sim 5 \times 10^{-3}$ A/cm^2 orders of magnitude higher than that in static SIMS (typically 10^{-9} A/cm^2 [1]). Thus, the surface and subsurface areas of the sample were in a highly dynamic state under Cs^+ bombardment; Pd and H atoms would have chemically reacted through a dynamical process, most likely atomic mixing, at the ion-impacted surface and/or subsurface.

A less understandable fact in Fig. 3 is that the relative intensity of signal G at *m/z* 106 is close to the relative abundance of ^{106}Pd. This means that the ion species at *m/z* 106 was mostly $^{106}Pd^-$, involving little $^{105}PdH^-$ ions; the formation process of PdH^- ions might have involved an isotope effect.

Another less-understandable fact is that dimers were emitted only as negative ions. A typical example of the kind is shown in Fig. 5, revealing rather intense dimer signals. This mass region was entirely signal free in the positive mode, implying that the dimer-ion emission restricted itself to the negative mode. For other elements, such as Si, Al, and Cu, cluster signals were always observed in the positive mode, as well as in the negative mode [13]. Nonemission of positive dimers was therefore peculiar to Pd/Cs^+.

The intensity distribution of negative dimer signals in Fig. 5 agreed well with the abundance distribution of natural-isotope dimers determined from the possible combinations of monomer isotopes. In addition, this spectral structure was little affected by deuterium gases introduced intentionally; the spectral structure of negative dimers was independent of residual hydrogen.

To date, two mechanisms have been proposed for cluster ion emission in SIMS: direct emission from the surface [14] and ion–atom recombination in the free space near the surface [15]. Traditionally, the latter mechanism has been regarded as probable for the emission of small cluster ions from elementary metal surfaces. Recently, however, the former mechanism has been shown to generate positive dimers and trimers of Al and Si [16]. In our case, no dimer ions were detected in the positive mode, assuring us that the sputtered positive ions did not recombine with sputter-ejected Pd atoms. It is quite improbable that neutral species selectively recombined with negative Pd ions in the gas phase, so we may affirm that negative dimer ions were emitted through the former mechanism.

Finally, there is no doubt that Cs^+ ions were neutralized upon colliding with the surface. Because resputtering of Cs^+-bombarded samples with O^+ invariably yielded an intense Cs^+ signal, neutralized Cs^+ ions were evidently adsorbed on or shallowly implanted beneath the surface. Because of their electro-positive nature, these adsorbed and implanted Cs atoms might have behaved as electron donors and hence lowered the surface work function [17] to favor the formation of negative ions, including negatively charged dimers. To corroborate this hypothesis, the electron affinity of Pd, PdH, and Pd_2 must be precisely known, but no related data are currently available.

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