In Situ ^{119}Sn Conversion Electron Mössbauer Study of the Surface of Tin Layers as Deposited by an Electroless Process

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ABSTRACT

In situ ^{119}Sn conversion electron Mössbauer spectroscopy has been used to investigate the process of autocatalytic (electroless) tin deposition in a strong alkaline solution using a rotating disk. It is very likely that a tin(II) compound—probably some tin(II) hydroxide complex—is present at the surface during the Sn-metal depositing disproportionation reaction. The results obtained in a tin(II) solution with a *p*H of 6.1 indicate the presence at the surface of what is probably a tin(II) chloride compound.

Tin can be deposited on other metals (*e.g.*, copper) to produce a corrosion resistant or solderable coating. Such layers are usually made by immersion plating, electrodeposition, or dip-soldering. Immersion plating, which involves a replacement of the substrate metal by tin, is restricted to layers with a limited thickness. Autocatalytic plating gives the possibility of selective deposition of metals to unlimited thickness. It was found that autocatalytic tin deposition is possible by a disproportionation reaction (1), in which the oxidation of one tin(II) ion at the surface supplies the two electrons for the reduction of a second tin(II) ion to metallic tin. The metallization solution contains tin(II) chloride, sodium hydroxide, and sodium citrate at a temperature of about 70°C. Because the solution is stable for days, the disproportionation agent must be an active tin(II) complex on the growing surface. This active complex can be formed from an inactive tin(II) complex in the solution. Using Mössbauer spectroscopy, it should, in principle, be possible to identify the active tin(II) compound by means of the isomer shift (*IS*) and quadrupole splitting (*QS*).

It is advantageous to study surfaces with conversion electron Mössbauer spectroscopy (CEMS). This is a well-established technique for ^{57}Fe, but ^{119}Sn is also very suited for CEMS (2). The conversion electrons, emitted on deexcitation of the ^{119}Sn nuclei, have an energy of about 20 keV. Due to the small escape depth of these conversion electrons, only a surface layer with a thickness of about 1 μm is measured with about 2/3 of the electrons originating from the outermost 0.5 μm (3). Because the recoil-free fraction of SnO_2 is nine times that of β-Sn, this technique is very sensitive for thin surface oxide layers. For instance, the spectrum of a sample consisting of tin metal, covered with 100Å SnO_2, will consist of contributions of the oxide amounting to 30% (3). Kordesh *et al.* (4) have developed a new technique that allows CEMS on a continuously immersed electrode using a cell design similar to that reported by Rath and Kolb (5). The electrode is a disk with its lower half in the electrolyte and its upper half close to the conversion electron detector. The disk rotates slowly, in order to measure continuously a freshly reacted surface. A similar setup is used to investigate the above-mentioned process of autocatalytic tin deposition. We also examined the surface of tin layers immersed in a tin(II) solution with a *p*H of 6.1, a solution in which a tin(II) compound is also formed at the surface.

Experimental

The setup for *in situ* CEMS is shown in Fig. 1. A Teflon disk, on which a thin copper disk is mounted, is slowly rotated by a motor at a speed of 1/4 rpm. The lower half of the disk is immersed in a bath and its upper half is close to the conversion electron detector. This detector is a proportional counter using a He/4% CH_4 gas flow. The perspex box, in which the whole setup is mounted, is filled with helium gas. A radioactive source with 5 mCi ^{119m}Sn in a $CaSnO_3$ matrix is used, which emits γ-rays with an energy of 23.9 keV. All isomer shifts are against $CaSnO_3$, and the velocity was calibrated using a ^{57}Co source and a standard α-Fe foil. The average measuring time for one spectrum is two days. The copper disk has been connected to earth potential.

The copper disk, mounted on the Teflon disk, was pretreated in the following way: it was immersed for one minute at room temperature in a solution containing 55 volume percent H_3PO_4, 25 v/o HAc, 20 v/o HNO_3, and 0.5 v/o HCl, to remove the passive film on the copper surface. This pretreatment was followed by intensive rinsing with deionized water for 30s. The cleaned copper disk was then treated with a solution containing 0.02*M* tin(II) chloride, 0.6*M* thiourea, and 0.2*M* sulfuric acid for 10 min at room temperature. Copper ions are dissolved and tin metal is deposited. Such tin layers were used as substrates for autocatalytic tin deposition. After rinsing with deionized water for 15s, the substrate was placed in the solution for autocatalytic deposition at 70°C containing 0.33*M* tin(II) chloride, 3.85*M* sodium hydroxide, and 0.66*M* sodium citrate. Before the Mössbauer spectrum was measured, we waited a few hours in order to have a tin layer thickness of more than 3 μm so as to avoid contributions to the spectrum of tin atoms near the copper-tin interface.

We also measured a number of tin surfaces with a thickness of more than 5 μm using a solution containing 0.1*M* tin(II) chloride, 0.66*M* sodium citrate, and 0.08*M* sodium hydroxide. This solution has a *p*H of 6.1. All solutions were prepared with oxygen-free deionized water.

Results and Analysis of the Mössbauer Spectra

Before we measured with the rotating disk, we checked the effect on autocatalytic tin deposition of repeatedly bringing the surface of the disk in and out of the solution. The deposition process continues when the surface is reimmersed in the solution.

The conversion electron Mössbauer spectrum of a slowly rotating disk with its lower half in the metallization solution at 70°C is shown in Fig. 2a. After this spectrum was measured, the disk was stopped and again the Mössbauer spectrum was collected at room temperature, at which no disproportionation takes place (Fig. 2b). From this latter spectrum the Mössbauer parameters of SnO_2 and of metallic tin are obtained. In the literature, values of the *IS* of metallic tin vary between 2.55 and 2.65 mm/s. From our spectrum, we obtained for β-tin an isomer shift of 2.60 mm/s and a linewidth of 0.90 mm/s. The line belonging to SnO_2 was fitted with a single Lorentzian line with an *IS* of 0.00 mm/s and a linewidth of 1.1 mm/s. The statistics of the spectra were not good enough to resolve the quadrupole splitting of SnO_2. The spectrum obtained with the rotating disk has been analyzed using these parameters, and a good fit could only be obtained by taking two Lorentzian lines for the resonance near 2.5 mm/s: one line originating from β-tin, with the above-mentioned parameters, which are kept fixed during the fit, and a second line with an isomer shift of 2.2 mm/s and a linewidth of 0.8 mm/s. When we took just one Lorentzian line for the resonance near 2.5 mm/s, we obtained an isomer shift of 2.48 mm/s and a linewidth of

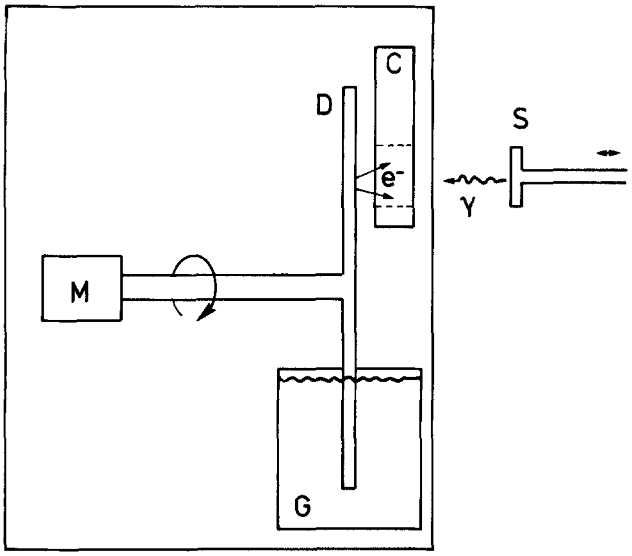

Fig. 1. Schematic diagram of the setup for *in situ* conversion electron Mössbauer spectroscopy. (M) Motor, (G) glass cuvet containing the tin(II) solution, (D) Teflon disk on which a thin copper disk is mounted, (C) conversion electron detector, (S) radioactive ^{119m}Sn source. The whole setup is mounted in a perspex box filled with helium gas.

1.1 mm/s. These parameters deviate significantly from those of β-tin.

In a similar way, we measured and analyzed the conversion electron Mössbauer spectrum of a disk that slowly rotated with its lower half in a tin(II) solution with a pH of 6.1 at room temperature. The line near 2.5 mm/s in the spectrum of the rotating disk could be analyzed using two Lorentzian lines: one originating from β-tin and a second line with an isomer shift of 2.9 mm/s and a linewidth of 0.8 mm/s (see Fig. 3a). The values of β-tin are obtained from the spectrum of the stationary disk (see Fig. 3b).

Discussion

Before we discuss the results, a number of experimental circumstances that could possibly account for the observed changes in the Mössbauer spectra must be considered: (*i*) to check whether the rotation itself could cause changes in the spectrum, we measured a copper disk covered with tin and observed identical spectra for the rotating and stationary disk; (*ii*) to check whether the presence of a thin layer of the solution could be responsible for the differences in the spectra, we took the same disk as mentioned in (*i*) and measured the spectra of the dry disk and of the disk rotating with its lower half in water, and again, identical spectra were found; and (*iii*) the decrease in temperature between the rotating disk (70°C) and the disk when it is stationary (25°C) causes an increase of the isomer shift of β-tin of 0.016 mm/s (6). This small temperature-dependent shift has been taken into account. We therefore conclude that the observed extra singlet in the conversion electron Mössbauer spectrum during the reaction is not an instrumental artifact but indicates the presence of a tin species at the surface during the disproportionation reaction. The measured Mössbauer parameters, IS = 2.2 mm/s and QS = 0 mm/s, are rather unusual for a tin(II) compound. It has been shown by a number of authors that tin(II) compounds can have isomer shifts as low as 1.8 mm/s, *i.e.*, in the tin(IV) region (7, 8). On the other hand, a tin(IV) compound with an isomer shift larger than 2.0 mm/s can be excluded (6).

The absence of a quadrupole splitting is more difficult to explain. It has been shown that tin(II) compounds with low isomer shifts often have a large quadrupole splitting (6). However, the quadrupole splitting strongly depends on the structure of the compound, in contrast to the isomer shift, which is not very sensitive to the structure. Most literature values of tin(II) compounds were obtained from powdered samples, whereas we measured thin surface layers on a wet disk. It has also been shown by Donaldson *et al.* that some tin(II) compounds, known to contain tin in lone-pair distorted sites, nevertheless have sharp singlet Mössbauer lines (9).

It is possible to obtain a small quadrupole splitting if we fit the observed spectra in a somewhat different way.

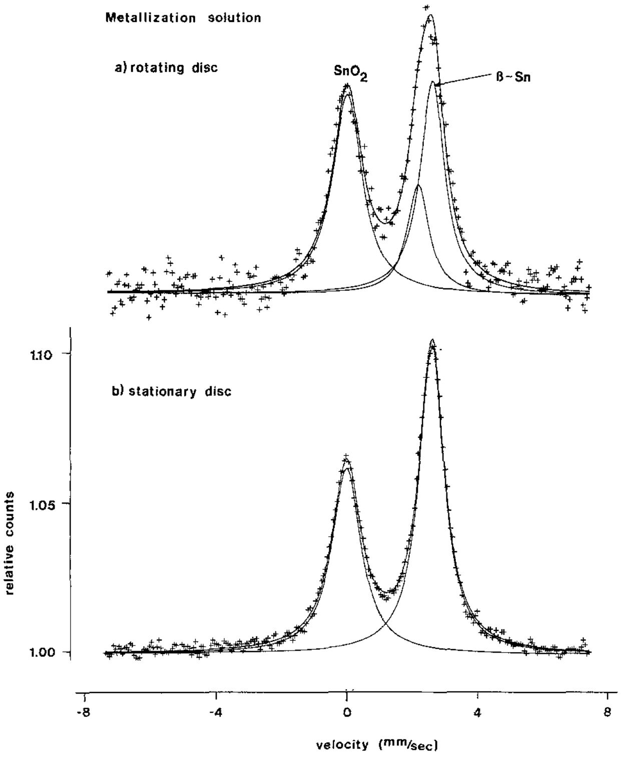

Fig. 2. (a) ^{119}Sn conversion electron Mössbauer spectrum of a rotating disk with its lower half in the metallization solution. (b) Mössbauer spectrum of the stationary disk.

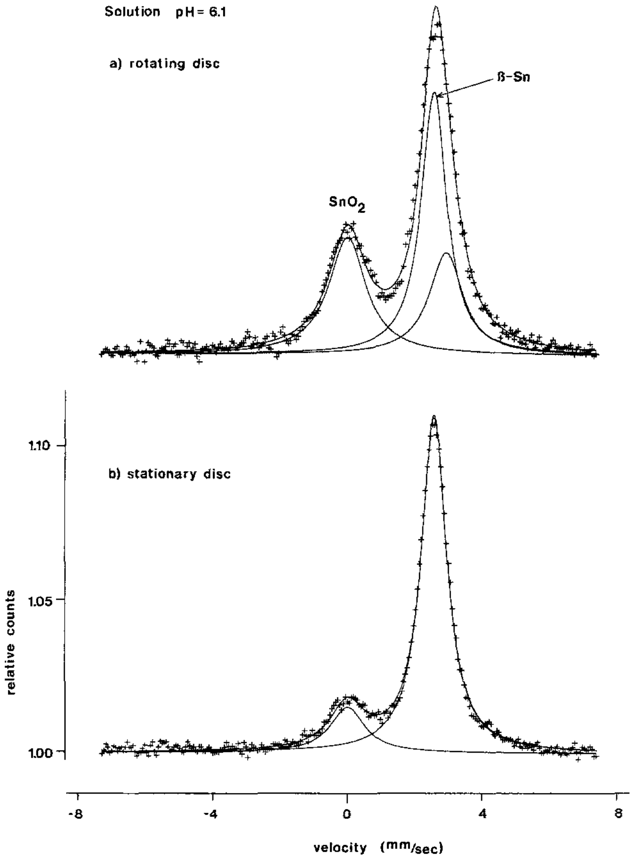

Fig. 3. (a) ^{119}Sn conversion electron Mössbauer spectrum of a rotating disk with its lower half in the tin(II) solution with a pH of 6.1. (b) Mössbauer spectrum of the stationary disk.

It is known that some tin compounds, especially when adsorbed on a surface, can exhibit the Gol'danskii-Karyagin effect due to anisotropy of the recoilless fraction (10, 11). In a quadrupole split spectrum, this effect will result in a difference in intensity between the two lines of the doublet. With increasing temperature, this effect becomes even more pronounced, and the intensity ratio of the two lines can be as high as 2.5 (12). Bearing this in mind, we fitted the spectrum of the rotating disk with one singlet originating from β-tin and a doublet with IS = 2.5 mm/s, QS = 0.6 mm/s, and an intensity ratio of the two lines of 2. This type of analysis and that previously described yielded equally good fits. As a third possibility, the spectrum can be fitted assuming that the observed extra singlet during rotation of the disk is the high-velocity component of a doublet with a quadrupole splitting of 2.2 mm/s, with its low-velocity component hidden under the SnO_2 peak around 0.0 mm/s. This doublet must then be assigned to a tin(IV) compound, since it has an isomer shift of about 1.2 mm/s. We now have three possibilities to fit the observed spectrum of the rotating disk all of which are mathematically equivalent: (*i*) SnO_2, β-Sn, and a singlet with IS = 2.2 mm/s and QS = 0 mm/s; (*ii*) SnO_2, β-Sn, and a doublet with IS = 2.5 mm/s and QS = 0.6 mm/s; and (*iii*) SnO_2, β-Sn, and a doublet with IS = 1.2 mm/s and QS = 2.2 mm/s. It is, however, very unlikely that a tin(IV) compound will not be present after the rotation of the disk has stopped, when it is present during the rotation. It is also very unlikely that only a tin(IV) compound is present during the rotation and no tin(II) compound. Although the Mössbauer parameters do not correspond to those of a known tin(II) compound, the value of the isomer shift points to the presence of a tin(II) compound at the surface during the disproportionation reaction.

The observed extra singlet, measured during the rotation of the disk with its lower half in a solution with a *p*H of 6.1, also points to the presence of a tin(II) compound. The value of the isomer shift of 2.9 mm/s is very close to the value reported by Cohen and West (13) who studied tin-palladium sols. They observed an extra singlet, with IS = 2.7 mm/s and QS = 0 mm/s, which cannot be ascribed to any known tin(II) compound. They attributed this singlet to Sn^{2+} ions, probably giving $(SnCl_3)^-$ complexes, which form a stabilizing layer surrounding palladium sol particles.

We will now discuss the possible tin(II) compounds, which may be present at the surface of the disk during the reaction. The effect of chloride ions in the metallization solution on the autocatalytic process has previously been studied. Both a metallization solution made with tin(II) chloride and a solution without chloride ions made by oxidation of metallic tin gave the same deposition rate on a catalytic surface. A tin(II) chloride compound as the disproportionating agent on the tin surface can, therefore, be excluded. It is suggested in Ref. (1), using thermodynamic arguments, that some tin(II) hydroxide complex or hydroxo-bridged tin(II) species may be present at the surface during the disproportionation reaction. It is probable that some tin(II) chloride compound is present at the surface of the disk when it is immersed in the solution with a *p*H of 6.1. This possibility is supported by the observations of some authors that tin(II) chloride hydroxide has an isomer shift that is at least 0.4 mm/s larger than that of tin(II) hydroxide oxide (14, 15).

Finally, as regards the amount of tin(II) compound present, it is known that tin(II) oxides have a recoil-free fraction that is about nine times that of β-tin (2). It is also known that our tin surfaces are fairly rough, giving rise to a large effective surface area. This means that only a few atomic layers of the tin(II) compound are likely to be present (3).

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