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Mössbauer Spectroscopy of ^{119}Sn Probe Cations on the Surfaces of ZnO Crystallites: Valence State, Local Environment, and Hyperfine Interactions of Tin Additives

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Abstract—A synthesis procedure that allows us to obtain ZnO:0.3 at % ^{119}Sn samples with Sn^{2+} ions on the surfaces of oxide particles containing structure-forming cations on tetrahedral sites is developed for the first time. Analysis of the ^{119}Sn Mössbauer spectra of obtained samples does not confirm the existence of the localized magnetic moments at ZnO grain boundaries recently suggested in the literature.

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INTRODUCTION

In [1], we showed that the annealing in hydrogen of a number of oxides originally containing impurity additives Sn^{4+} in the volume of particles allowed us to localize ^{119}Sn probe nuclei in surface positions and thus use ^{119}Sn Mössbauer spectroscopy for characterization of physical and chemical processes at the solid–gas interface. The oxides suitable for this purpose had different crystalline structures, but the cations in all of them were in coordination polyhedrons of $[MO_6]$ octahedral type. The question of stabilizing ^{119}Sn on the surfaces of compounds containing cations in polyhedrons of other types therefore remained open. The aim of this work was to study Mössbauer spectra of ^{119}Sn probe cations in the structure of hexagonal zinc oxide, which contains metal atoms $[ZnO_4]$ tetrahedral groups. Numerous works have been devoted to studying this compound, the main component of thin films with promising optoelectronic properties [2]. Additional interest in the study of zinc oxide, which exhibits diamagnetic properties in the coarse grain condition, has recently arisen in connection with the unexpected detection of weak ferromagnetism of its nanograin samples [3].

EXPERIMENTAL

The co-precipitation of Zn(II) and Sn(IV) hydroxides by aqueous ammonia added to mixtures of aqueous solutions of $ZnCl_2$ and $^{119}SnCl_4$ until pH 8.0–8.5 is attained was used to synthesize polycrystalline ZnO samples with 0.3 at % Sn^{4+} in the bulk of crystallites.

The precipitate (precursor) was filtered and thoroughly washed on the filter with water, which also displayed a slightly alkaline reaction created by the addition of a few drops of ammonia solution. X-ray phase analysis of ZnO powder obtained by annealing the precursor in air for 2 h at 600°C (substance 0) showed it was single phase, and its particles had a wurtzite-type crystalline structure (space group P63mc).

To synthesize samples containing ^{119}Sn probe nuclei in positions on the surfaces of crystallites, a part of powder 0 was transferred into a quartz reactor and heated in a current of H_2 (6 h at 310 ± 10°C). These conditions of reduction were selected based on the procedure used earlier for synthesizing TiO_2:0.3 at % Sn^{4+} samples [4], which allowed the most of Sn^{4+} ions, that were located in the bulk of crystallites, to move towards their surfaces. The powder (substance **1**) annealed in the reactor, which was still kept in the H_2 atmosphere, was then characterized by in situ ^{119}Sn Mössbauer spectroscopic measurements. A part of material **1** was brought into contact with air (material **2**) and analyzed by x-ray photoelectron spectroscopy (XPS). ^{119}Sn Mössbauer spectra were recorded on an MS-1104 spectrometer with a $Ca^{119m}SnO_3$ source. During the measurements, both the source and absorber were kept at 100 K. Standard software was used to process the spectra. The values of isomer shift are given relative to a $CaSnO_3$ reference absorber. XPS measurements were performed on a *K*-Alpha X-Ray photoelectron spectrometer with an AlK_α monochromatic radiation source ($h\nu$ = 1486.6 eV). The atomic ratio [Sn]/[Zn] was determined from the

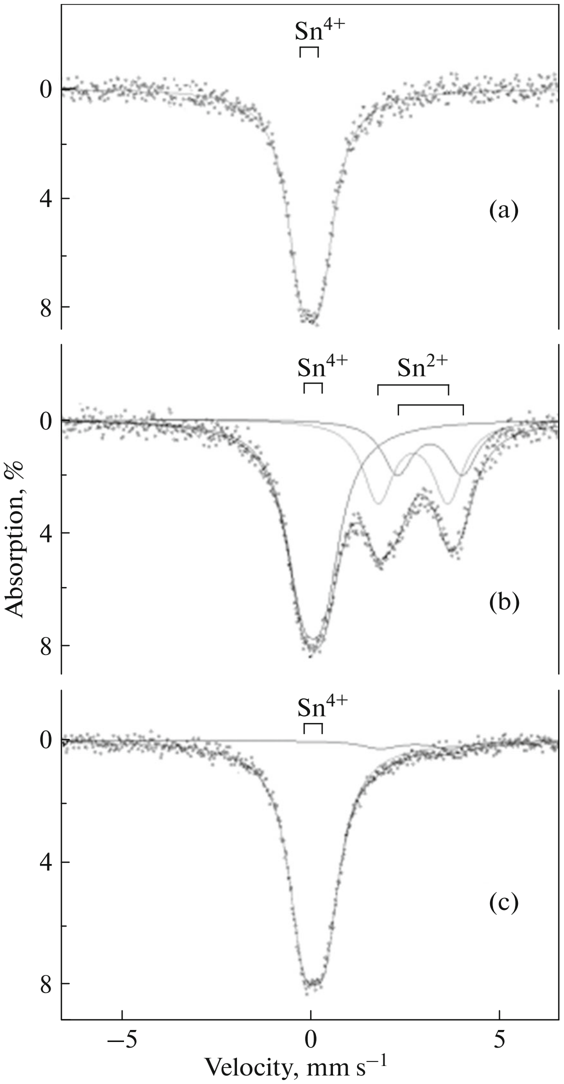

Fig. 1. ^{119}Sn Mössbauer spectra of our ZnO:0.3 at % Sn samples: (a) spectrum of the initial sample prepared by annealing the hydroxide precursor in air for 2 h at 600°C (substance 0); (b) spectrum of sample 1 obtained in situ (substance 0 heated in hydrogen for 6 h at 310°C); (c) spectrum obtained after heating sample 1 in air for 1 h at 200°C (substance 2).

areas of the peaks of Sn3*d5* (bonding energy E_b = 487 eV) and Zn2*p3* (E_b = 1022 eV), taking into account the relevant Scofield's corrections.

RESULTS AND DISCUSSION

Analysis of the ^{119}Sn Mössbauer spectrum of initial substance **0** (Fig. 1a) revealed the presence of a single component: an unresolved doublet (D0) with the following parameters (see Table 1): isomer shift δ = 0.04 ± 0.03 mm s^{-1}, quadrupole splitting ΔE_Q = 0.55 ± 0.05 mm s^{-1} and FWHM Γ = 0.91 ± 0.05 mm s^{-1}. These values show that the tin atoms in sample **0** were in the oxidation state +4 and occupied the same structural positions characterized by the somewhat distorted symmetry of the local atomic environment. It is noteworthy that the values of the spectral parameters of ^{119}Sn in the investigated substance were close to those observed in [1] for Sn^{4+} in oxides with cations in the polyhedrons of octahedral symmetry. In situ ^{119}Sn Mössbauer measurements performed after annealing substance **0** in H_2 showed (Fig. 1b) that the unresolved doublet in Fig. 1a was nevertheless not associated with Sn^{4+} outside the structure of ZnO.

A doublet with δ = 2.70 mm s^{-1} and ΔE_Q = 1.33 mm s^{-1} would in this case have to be in Fig. 1b, reflecting the transition of tin to the divalent state with the formation of a thermodynamically stable tetragonal modification of SnO [5] and/or a single peak with δ = 2.55 mm s^{-1} and $\Delta E_Q \leq 0.3$ mm s^{-1}, indicating the full reduction of tin to β-Sn. Despite this, however, analysis of the spectrum in (b) (see Table 1) showed that it was a superposition of three doublets, none of which had parameters consistent with those given above for the tetragonal modification of SnO.

Within the error of measurement, the parameters of doublet DI coincided with the parameters of original doublet D0 in Fig. 1a, suggesting that nearly half of the Sn^{4+} impurity ions remained in their original oxidation state after heating in hydrogen, as expected when these ions are present in the bulk of ZnO crystallites. At the same time, the lack of resonant absorption peak at velocity υ = 2.55 mm s^{-1} showed that under our experimental conditions, there was no reduction of Sn^{2+} ions supposedly capable of transforming to the elementary β-Sn state.

Even though the values of the parameters of doublets DII and DIII (see table) do not allow them to be attributed to tetragonal SnO, and they therefore also contradict the presence of clusters SnO_2 in sample **0**, both doublets nevertheless correspond to covalent forms of divalent tin with a $5s^{2-x}5p^x$ electronic configuration, according to [6]. The mixing of *s* and *p* states in this case explains the values of $\delta_{(II)}$ and $\delta_{(III)}$, which are much lower than expected for purely ionic configuration $5s^25p^0$ ($\delta \geq 4$ mm s^{-1}) due to the decrease in total electron density $|\Psi(0)|^2$ on ^{119}Sn nuclei due to the shielding effect produced by 5*p* electrons.

In addition, the high values of ΔE_Q corresponding to doublets DII and DIII indicate substantial gradients of the electric field acting on the ^{119}Sn nucleus, and thus on the nonspherical distribution of the electric charge in the hybridized valence orbitals of Sn^{2+}. This means that the two above forms of ^{119}Sn^{2+} contain a stereochemically active unshared pair of 5*s* electrons, indicating they occupy sites of low coordination numbers that are consistent with the presence of Sn^{2+} on the surfaces of crystallites. An additional argument that the emergence of doublets DII and DIII was due

Table 1. Parameters of ^{119}Sn Mössbauer spectra of polycrystalline samples of tin-doped wurtzite ZnO:0.3 at % Sn

Sample	δ, mm s^{-1}	ΔE_Q, mm s^{-1}	Γ, mm s^{-1}	A, %
0 (initial sample (Fig. 1a))				
D0	0.04 ± 0.03	0.55 ± 0.05	0.91 ± 0.05	100
1 (sample **0**, heated in H_2 (Fig. 1b))				
DI	0.06 ± 0.03	0.55 ± 0.05	1.05 ± 0.05	54 ± 4
DII	3.13 ± 0.05	1.71 ± 0.06	0.96 ± 0.08	18 ± 4
DIII:	2.70 ± 0.04	1.85 ± 0.06	0.96 ± 0.08	28 ± 4
2 (sample **1**, heated in air (Fig. 1c))				
DIV	0.06 ± 0.03	0.56 ± 0.05	0.95 ± 0.05	90 ± 5
DV	⟨2.91⟩	⟨1.78⟩	1.00	10 ± 5

to the bulk-to-surface migration of ^{119}Sn is that the values of their parameters within the error of measurement coincides with those observed for ^{119}Sn^{2+} ions on TiO_2 surfaces, distributed over two nonequivalent positions as in the case of ZnO [4].

Further experiments showed that exposure to air for 1 h at 200°C was sufficient to oxidize most of the Sn^{2+} ions formed in sample **1** (Fig. 1c), testifying to their easy accessibility to molecules of oxygen. Since contact between sample **1** and air at this temperature could only slightly reduce the number of surface tin atoms (as a result of some of the Sn^{4+}ions, formed in sample **2**, to the bulk of particles), this allowed us to verify the location of the tin on the surfaces of this sample's particles by means of XPS. Comparing the $([Sn]/[Zn])_{XPS}$ ratios, corresponding to surface layers 3–5 nm thick, showed that heating sample **0** in H_2 considerably enriched the surface with tin atoms ($([Sn]/[Zn])_{XPS}$ = 0.014 and 0.036 for **0** and **2,** respectively).

CONCLUSIONS

Our data showed for the first time that Mössbauer ^{119}Sn probe nuclei can be localized on the surfaces of oxide particles containing metal atoms in non-octahedral polyhedrons. It should be noted that the Mössbauer spectra of the ZnO:0.3 at % Sn samples studied in this work did not allow us to detect the participation of surface cations of tin in magnetic hyperfine interactions of ^{119}Sn, regardless of the oxidation state of tin dopant. This indicates a lack of localized magnetic moments in the environment of surface cations of tin, the detection of which would confirm the assumption in [7] on the crucial role of grain boundaries in the processes responsible for the emergence of ferromagnetism in highly dispersed samples of zinc oxide.

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