

Research Article

Hydrogen Charging Effects in Pd/Ti/TiO₂/Ti Thin Films Deposited on Si(111) Studied by Ion Beam Analysis Methods

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Titanium and titanium dioxide thin films were deposited onto Si(111) substrates by magnetron sputtering from a metallic Ti target in a reactive Ar+O₂ atmosphere, the composition of which was controlled by precision gas controllers. For some samples, 1/3 of the surface was covered with palladium using molecular beam epitaxy. Chemical composition, density, and layer thickness of the layers were determined by Auger electron spectroscopy (AES) and Rutherford backscattering spectrometry (RBS). The surface morphology was studied using high-resolution scanning electron microscopy (HRSEM). After deposition, smooth, homogenous sample surfaces were observed. Hydrogen charging for 5 hours under pressure of 1 bar and at temperature of 300°C results in granulation of the surface. Hydrogen depth profile was determined using secondary ion mass spectrometry (SIMS) and nuclear Reaction Analysis (N-15 method), using a ¹⁵N beam at and above the resonance energy of 6.417 MeV. NRA measurements proved a higher hydrogen concentration in samples with partially covered top layers, than in samples without palladium. The highest value of H concentration after charging was about 50% (in the palladium-covered part) and about 40% in titanium that was not covered by Pd. These values are in good agreement with the results of SIMS measurements.

1. Introduction

Titanium hydride films have many potential applications, for example, neutron super mirrors (multilayers of nickel and titanium employed for the transport of cold neutron beams), hydrogen storage layers, and standards for hydrogen quantitative analysis. Saturation of these systems with hydrogen improves their reflectivity, because hydrogen increases the difference between the two indices of refraction and allows one to diminish the number of layers needed [1]. In addition, titanium deuteride films can be employed as a neutron source in ion beam technology.

Titanium and its alloys have many industrial applications thanks to their excellent corrosion resistance and high specific strength. However, hydrogen absorption induces cracking of titanium layers (hydrogen-induced cracking, HIC) because of hydrogen absorption [2]. Titanium dioxide top layers act as a protective layer (against corrosion) but also as a barrier to hydrogen absorption into the metal [3].

The mechanism by which the oxide influences hydrogen permeation into Ti and its alloys is still not well established, but it is known that diffusion of hydrogen in TiO₂ is slower than that in the pure metal [4, 5]. Additionally, the atomic transport can be improved using palladium layers. Some

theoretical models, in particular based on finite elements method, have been used to simulate the behavior of hydrogen in titanium oxide layers [3]. Titanium is also one of the most important elements that can store high amounts of hydrogen so titanium alloys as well as thin films are taken into consideration as candidate for engine fuels [6]. Therefore, it seems to be straightforward to study physical properties as resistivity, surface topography in titanium, and in titanium oxide-hydrogen systems, as it is reported in this paper. Additionally, hydrogen profiles and its diffusion through the different layers have been studied.

2. Experimental Methods

Deposition process was carried out in a planar, magnetron sputtering system described in detail elsewhere [7, 8]. Magnetron discharge was driven by a d.c. pulse power supply. Substrates for film deposition were placed on a rotatable holder above the target. The substrate holder was completely covered by a shutter with a 20×30 mm window permitting deposition onto substrates at one of 8 different positions. The target to substrate distance was 35 mm. *In situ* substrate heating up to 300°C was provided. Temperature control was performed using a Pt 100 thermoresistor, mounted directly into the substrates holder.

The target of 5N Ti was sputtered either in high purity argon (for Ti layer deposition) or Ar+O₂ reactive gas atmosphere, the composition of which was controlled by MKS mass-flow meters (in the case of TiO₂). The films were deposited onto Si(111) substrates at 250°C . The thickness of the layers was controlled by the deposition time.

After titanium and titanium dioxide layers deposition, some of the samples were partially (1/3 of the surface) covered by 20 nm thick palladium layer by physical vapour deposition (PVD). The thickness of the deposited layers was controlled *in situ* using a quartz crystal microbalance. In the case of 20 nm palladium layers, the time of deposition was 1400 s, the process took place in ultrahigh vacuum ($1.5\text{--}6.0 \times 10^{-9}$ mbar).

RBS measurements were performed at the Institute of Nuclear Physics of the University Frankfurt/Main, using a 2 MeV 4He⁺ ion beam with 171° backscattering angle. Details of the experimental conditions have been published elsewhere [9]. For data evaluation the computer code SIMNRA [10] was used taking into account the electronic stopping power data by Ziegler and Biersack, Chu+Yang's theory for electronic energy-loss straggling, and Andersen's screening function to Rutherford cross-section. The contribution from a double and/or multiple scattering into the RBS spectra [11] was taken into account using the calculating facilities of SIMNRA. It is more convenient to have the estimated layer thickness in nm. Thus, the simulated RBS area density values (10^{15} atom/cm²) were converted into the layer thickness value (nm) by using the mass density of the bulk Ti (4.51 g/cm^3) and/or taking into account the mass density of TiO₂ (4.25 g/cm^3) for the samples containing titanium oxide layer. We note here that the real thickness of layers could be somewhat different, since they could have a slightly different

mass density as that of the bulk sample. Besides, the sputter deposited films have some porosity, and thus the mass density of the film is certainly lower than that of the bulk one.

SIMS, resistivity and electron microscopy measurements were performed at the Institute of Materials Science of Technische Universität Darmstadt. SIMS measurements were performed using Cs⁺ primary ions recording positive secondary ions by a CAMECA ims 5f equipment with a base pressure of 3×10^{-10} mbar. For the resistivity measurements, the 4-point method was used. The applied current was in the ranges 1–100 mA. High Resolution Scanning Electron Microscopy measurements were performed using a Philips XL 30 FEG microscope with field emission electron gun.

N-15 nuclear reaction analysis (NRA) measurements were performed at the Dynamitron Tandem Laboratorium of the Ruhr-Universität Bochum. The reaction $^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + \alpha + \gamma$ (4.965 MeV) with a resonance at 6.417 MeV was used to obtain the results. For data evaluation the computer code SRIM was used.

Two series of samples have been charged with hydrogen at the same temperature (300°C) and pressure (1 bar), but for different times. Sample from the first series (Pd/Ti/TiO₂/Ti/Si) was charged twice, for 5 and for 15 hours (20 hours in total). Sample from the second series (Ti/TiO₂/Ti/Si) was charged three times, for 2 hours, for 3 hours (5 hours in total), and additionally for 3.5 hours (8.5 hours in total).

3. Results and Discussion

3.1. Composition. Prior to other experiments the composition of samples was studied by RBS. The compositions and the fitted values of layer thicknesses have been in good agreement with the nominal values. Figure 1 shows the fitted spectra for two different samples. The spectra show clearly that there is no interdiffusion at the interfaces (Table 1).

3.2. Surface. The chemical composition of the Ti surface layer, with and without Pd, was determined by Auger electron spectroscopy (AES) with energy of primary beam 3 keV. In both spectra the peak at energy of 271 eV corresponds to carbon impurity; in titanium layer also some oxygen is present (peak at 512 eV), as shown in Figure 2.

The topography of titanium and palladium layers was studied by High Resolution Scanning Electron Microscopy. In both cases, we observed smooth and homogenous layers, without any islands or granulations (Figure 3(a)). After hydrogen charging, granulation of titanium surface was observed (Figure 3(b)), as it was described by Nakao et al. [12]. Surface of palladium layer was not changed by increasing the amount of hydrogen in the layer. Nevertheless, some cracks were observed, because of the elevated charging temperature of 300°C .

3.3. Resistivity. H in transition metals, like Ti, tends to occupy tetrahedral interstitial sites. As it is well known from the literature [13], one can reach the best solubility of H in

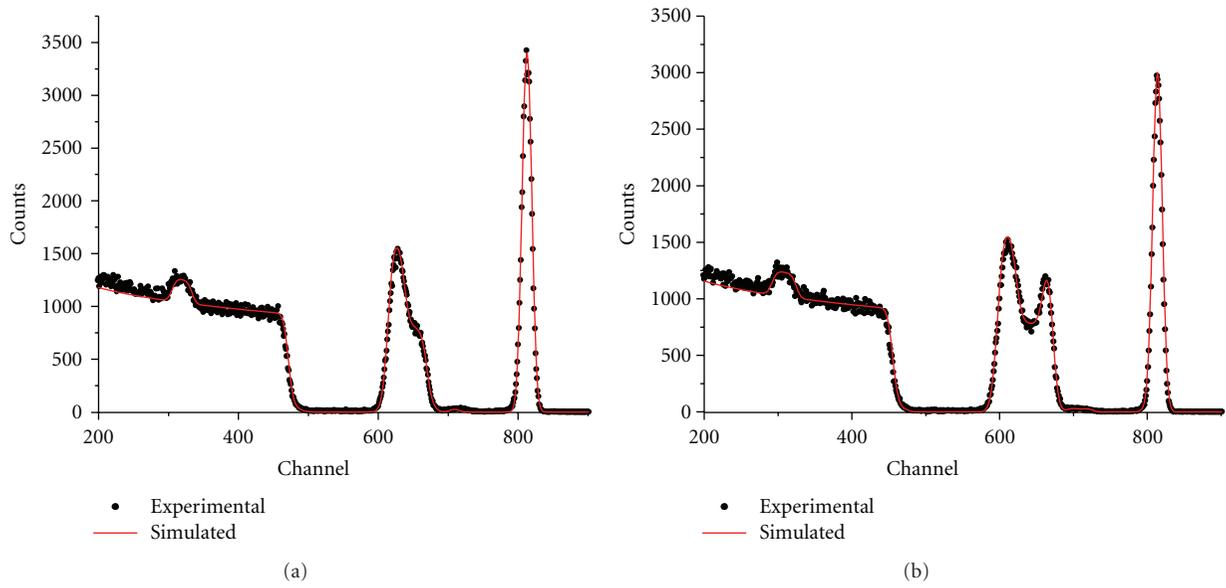


FIGURE 1: Measured (markers) and fitted (red line) RBS spectra for (a) Pd/TiO₂/Ti and (b) Pd/Ti/TiO₂/Ti films deposited on Si (111).

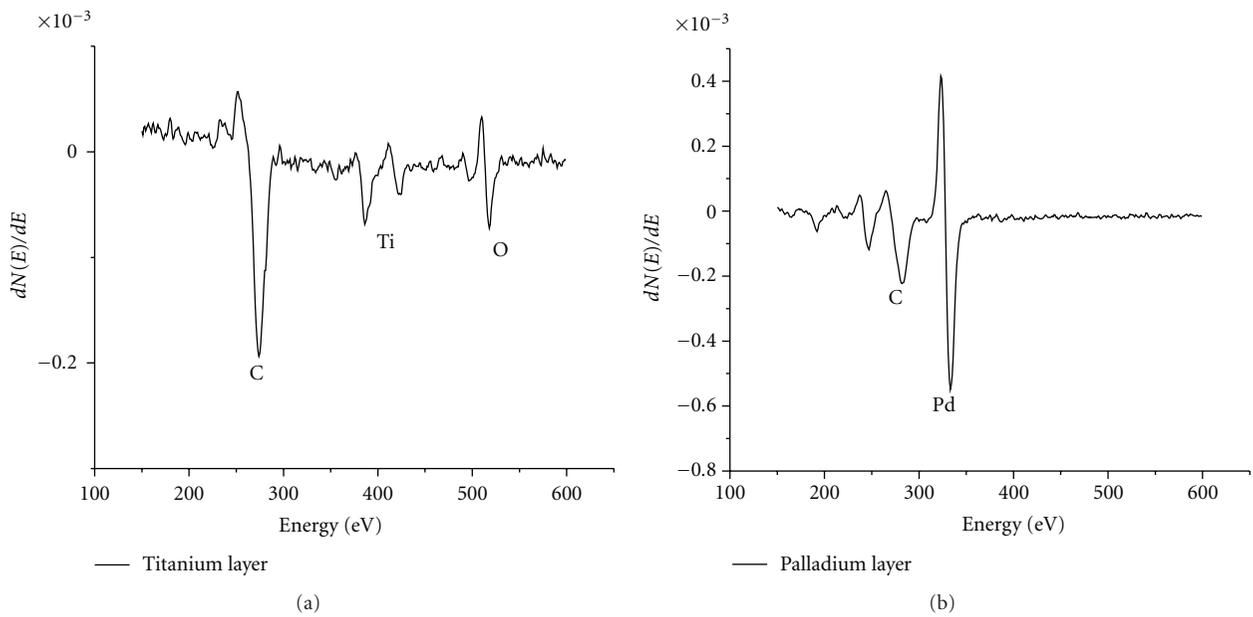


FIGURE 2: AES spectra for (a) titanium and (b) palladium layer.

TABLE 1: Thicknesses of the samples, nominal and obtained from RBS measurements.

	Pd/TiO ₂ /Ti/Si(111)		Pd/Ti/TiO ₂ /Ti/Si(111)	
	Nominal thicknesses	RBS thicknesses	Nominal thicknesses	RBS thicknesses
Pd	20 nm	20 nm	20 nm	19 nm
Ti	—	—	50 nm	40 nm
TiO ₂	100 nm	97 nm	100 nm	96 nm
Ti	100 nm	79 nm	100 nm	80 nm

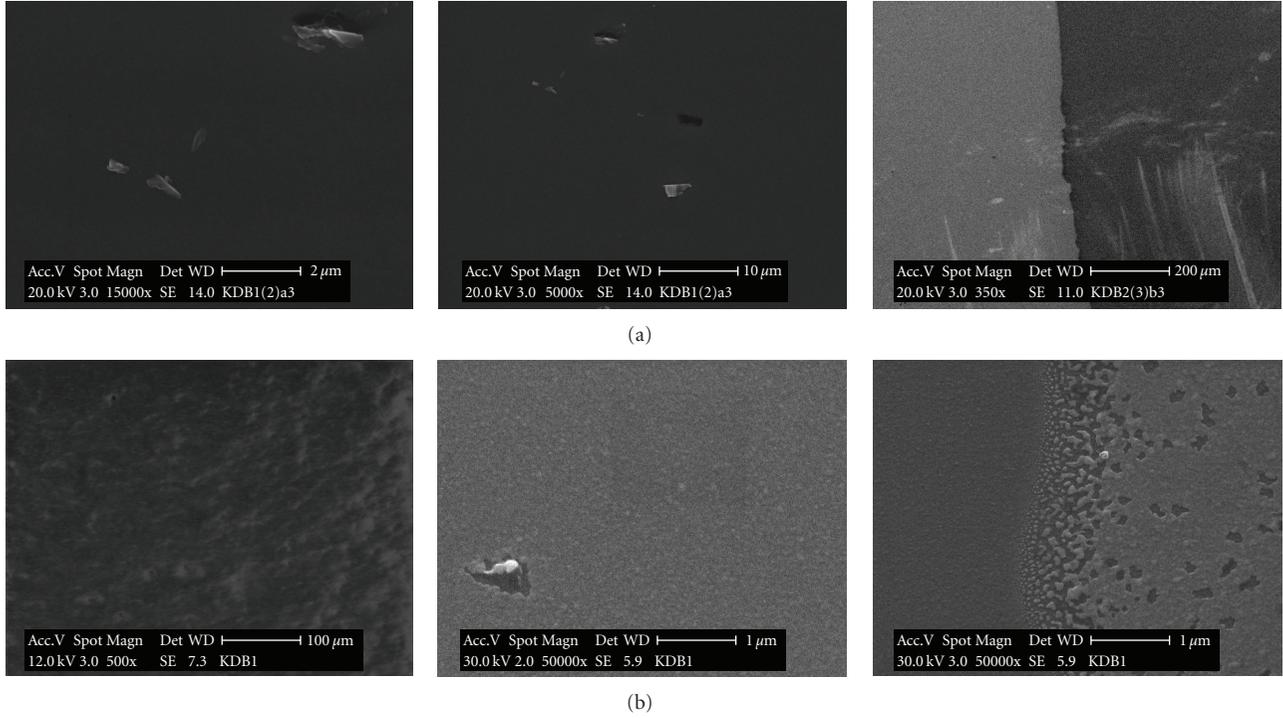


FIGURE 3: HRSEM images for a series of samples with titanium top layers and the boarder between titanium and palladium for samples partially covered by Pd before (a) and after (b) hydrogen charging.

the case of the β -phase (12 tetrahedral and 6 octahedral interstitial positions). The solubility of hydrogen in α -titanium is quite negligible [13]. For small amounts of hydrogen in titanium (α -Ti), hydrogen forms a disordered interstitial solution in the HCP Ti lattice (only 4 tetrahedral interstitial sites), and hydrogen atoms act as extra scattering centers for the conduction electrons. Therefore, the resistivity of the layer will be increased. Hydrogen atoms in titanium represent a model system for concentrated lattice gas [14]. This system is an ideal physical realization of this model because of the wide ranges of hydrogen solubility and the high mobility of hydrogen in Ti. Therefore, it can be described using the lattice gas automata (LGA) or lattice gas cellular automata (LGCA) methods.

With increasing amount of hydrogen in the sample, titanium hydride with H-vacancies (under stoichiometric composition) will be created (FCC lattice), and hydrogen atoms will occupy tetrahedral voids, so the contribution of conducting electrons becomes larger than the contribution of scattering centres in the lattice. Consequently, the resistivity will be decreased [15].

Resistivity of the top titanium layer was measured for each sample using the 4-point method and was calculated using the equation

$$\rho = \frac{\pi}{\ln 2} \times d \times \frac{U}{I}, \quad (1)$$

where d is the thickness of the titanium layer, U is the measured voltage, and I is the applied current. Before hydrogen

charging, the measured average resistivity for each sample was in good agreement with the literature.

The resistivity measured on the titanium layer of the sample Pd/Ti/TiO₂/Ti/Si (on the area that was not covered with palladium) before hydrogen charging was found to be $1.76 \times 10^{-7} \Omega\text{m}$. After the first charging step, resistivity decreased to $1.21 \times 10^{-7} \Omega\text{m}$, and after the second charging step, the resistivity decreased again down to $0.98 \times 10^{-7} \Omega\text{m}$. Because of the conditions of hydrogen charging (at 300°C the concentrations of hydrogen in α , β , and δ (hydride) phases are 6.72, 39, and 51.9 at%, respectively [16]), we can state; that already after the first step of hydrogenation, the pure β -phase or at least a mixed ($\alpha + \beta$)-phase has been reached. The sharp decrease in the resistivity seems to confirm this statement. After the last charging step N-15 measurements have been performed. The results show a hydrogen concentration of over 50% in the titanium layer, meaning that probably the δ phase with FCC lattice has been achieved. Up to this region, Debye's temperature, as well as electronic specific heat coefficient, decrease linearly with increasing amount of hydrogen [17]. Obtaining higher H concentration values (over 60%) an "electronically driven" fcc \leftrightarrow fct transformation will be induced [18].

In the Ti/TiO₂/Ti/Si sample the resistivity measured prior to hydrogen charging was found to be $2.25 \times 10^{-7} \Omega\text{m}$. In both cases (samples with and without palladium) the value of resistivity is slightly under the literature value, probably because samples contained small amount of hydrogen already before hydrogen charging (the presence of H was confirmed by SIMS measurements). It is also visible from

Figure 4 that the resistivity is lower for samples covered by palladium (because of the supporting role of Pd for hydrogen dissociation and diffusion into the metal). However, later both curves are decreasing almost parallel. After the first charging step, it decreased to $2.17 \times 10^{-7} \Omega\text{m}$, after the second charging step it decreased to $1.88 \times 10^{-7} \Omega\text{m}$, and after the last charging it decreased to $1.63 \times 10^{-7} \Omega\text{m}$. This change in the resistivity suggests that after the first process of charging the $(\alpha + \beta)$ - or β -phase was achieved and after the second process the pure β -phase was obtained. Further N-15 measurements showed about 40% of hydrogen in the sample, meaning that in this case the δ phase has not been reached.

Because their resistance can be switched reversibly by an applied electric field, metal-insulator-metal (MIM) structures such as Ti/TiO₂/Ti have been proposed for resistive random-access memories (ReRAM) [19]. However, methods for improving the uniformity of resistive switching parameters will be yet studied. Yingtao Li et al. [20] reported nitrogen annealing as a method improving the broad variations of the resistive switching parameters in the as-deposited TiO_x films. Changing the resistivity of titanium by hydrogen charging could also be a way to modify properties of such systems.

3.4. Hydrogen Profiling. To obtain the hydrogen profiles in samples Pd/Ti/TiO₂/Ti/Si(111) and Ti/TiO₂/Ti/Si(111) with the same titanium layer thicknesses and the same hydrogen charging times and temperature, SIMS and N-15 measurements have been performed.

For those samples, partially covered by palladium, it is clearly visible that hydrogen charging enhanced the hydrogen concentration (storage) in both (top and bottom) titanium layers, but no changes were observed in the oxide layer.

Titanium is a metal that was widely investigated as a potential material for hydrogen storage, because of its high hydrogen storage capacity (67%) and its very low outgassing property [21]. In the titanium-hydrogen system, the heat of solution and the formation energy of the hydride, TiH₂, are both negative [22]. At elevated temperatures, hydrogen atoms in the titanium formed hydrides immediately. The hydride formation is therefore controlled by the diffusion process of the hydrogen atoms, and numerical calculations concerning this topic have also been performed, and some theoretical models have been developed [23, 24]. One of these models is based on the idea that complex defects will contribute to the surface diffusion flux at temperatures approaching the melting point and allows determining diffusion coefficient even in the case of very complex and defect-ed systems.

Results presented here show that after charging the concentration of hydrogen was increased in titanium layers; however, in the titanium dioxide layer its concentration remains the same as before (Figures 5 and 6(a)). Results of N-15 measurements show an accumulation of hydrogen in both titanium layers (up to 50%) but only a small amount (less than 5%) in the oxide layer. These results are in good agreement with results of SIMS measurements (Figure 6). It seems to be clear that hydrogen diffuses through the oxide

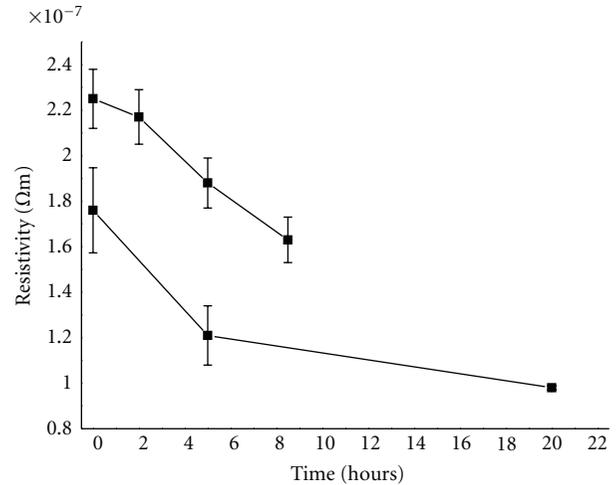


FIGURE 4: Charging time dependence of resistivity in titanium layer.

layer without any accumulation there. This fact can be explained by the mechanism, proposed by Bates et al. [25], who described the diffusion of hydrogen and its isotopes through a TiO₂ sample in direction parallel and perpendicular to the *c* axis. They showed that because of its large open channels parallel to the *c* axis, diffusion of hydrogen is very rapid in this direction and proceeds by a proton jump from one O²⁻ ion to another along this channel (so diffusion parallel to the *c* axis is much faster than in the perpendicular direction).

For a sample without palladium layer, the situation is quite similar and differs only in the contents of hydrogen. Prior to charging some amount of hydrogen was observed by SIMS measurements because of the H absorption of the surface. Charging with hydrogen increased this amount in the top titanium layer significantly, but in the second titanium layer the concentration of hydrogen remains lower than in the case of the sample with palladium top layer (Figure 7). This result indicates that palladium acts as a catalyst for gathering hydrogen in Ti and its diffusion through the TiO₂ layer.

Results of N-15 measurements show a high accumulation of hydrogen in the first titanium layer (~40%) and a smaller amount in the second titanium layer (~15%). Only a very small amount of hydrogen was observed in the oxide layer. This indicates that the lack of palladium on the top hinders hydrogen to penetrate into titanium, as well as into the second Ti layer through the titanium dioxide layer [3]. Pd supports the dissociation of H₂ molecules on the surface. Having Pd metal atoms on the surface, they can promote the dissociation of hydrogen molecules, and so the H atoms can be easily absorbed by the bulk of the metal and diffuse through other layers. These results are in good agreement with concentration depth profiles from SIMS measurements.

4. Summary

In this study, the main characteristics of hydrogen absorption by titanium and titanium dioxide thin films were investigated

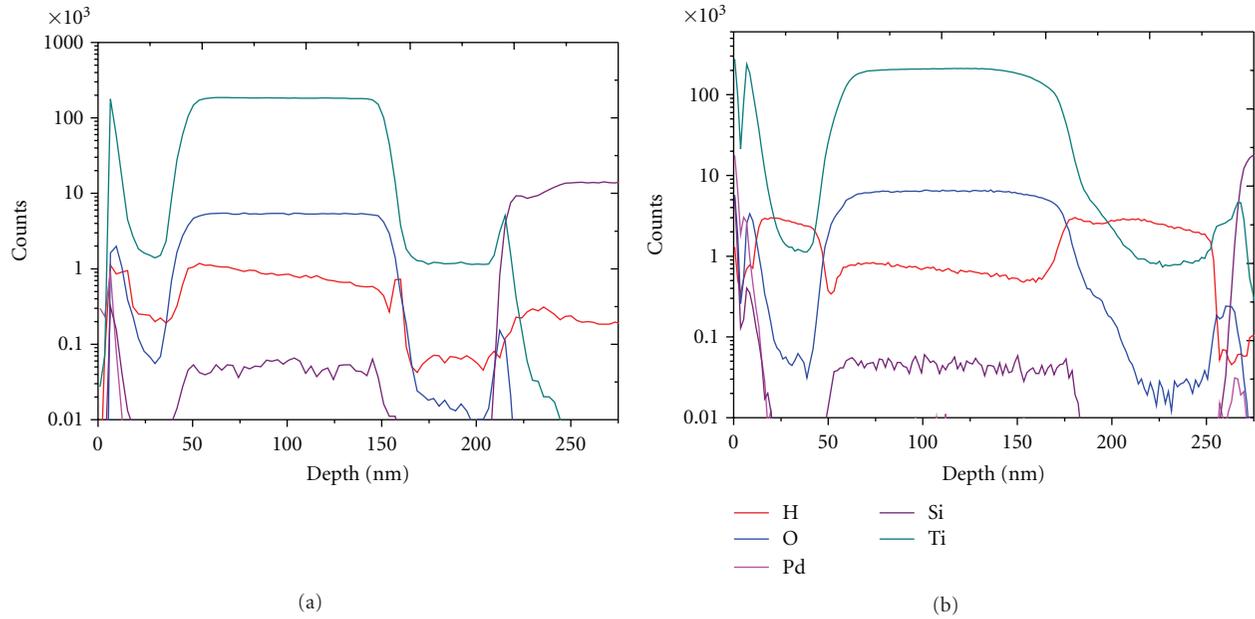


FIGURE 5: SIMS profiles for the sample Pd/Ti/TiO₂/Ti/Si before (a) and after (b) hydrogen charging.

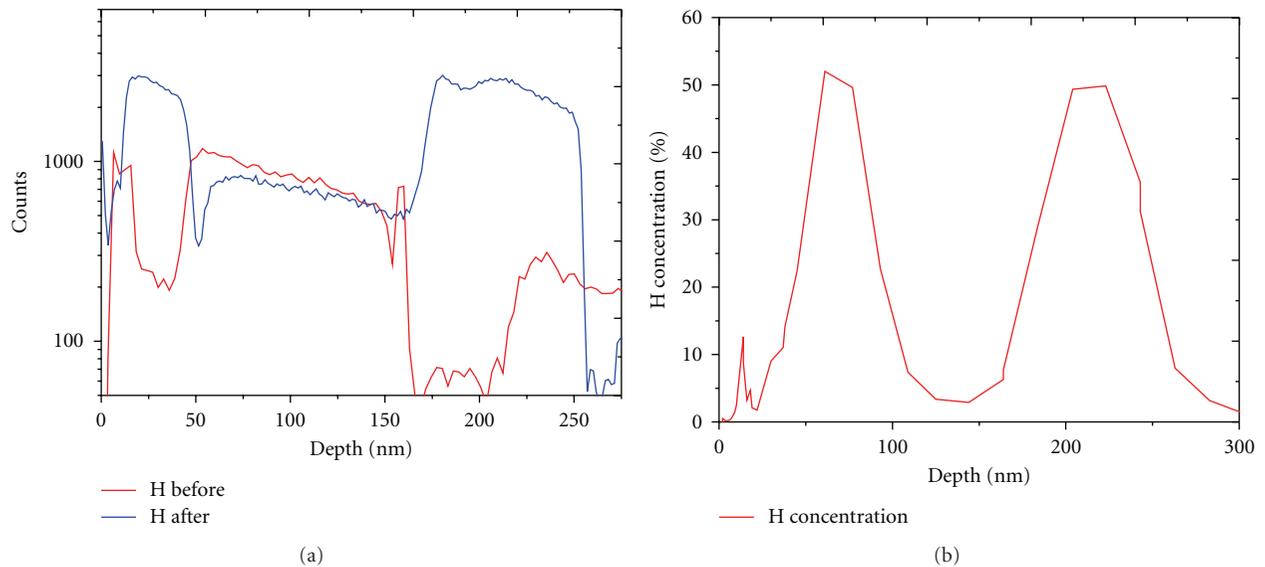


FIGURE 6: Comparison of H profiles for the sample Pd/Ti/TiO₂/Ti/Si measured by SIMS (a) and N-15 (b).

with specific emphasis on the hydrogen diffusion and its storage in each layer. It is clearly visible from the results that palladium acts as a catalyst for hydrogen diffusion through TiO₂ layer and increases the maximum H concentration up to a value of over 50% (under the palladium-covered part) instead of about 20% in titanium if it is not covered by palladium. Hydrogen profiles obtained both by SIMS and N-15 measurements proved this higher hydrogen concentrations in good agreement in samples with partially covered top layers. Concerning the surface, hydrogen charging caused a granulation of titanium layer. Also the palladium layer was changed (cracks on the surface) because of the elevated

temperatures during the hydrogen charging process. The resistivity of the samples has decreased with increasing hydrogen charging according to the predictions as it was pointed out in the discussion.

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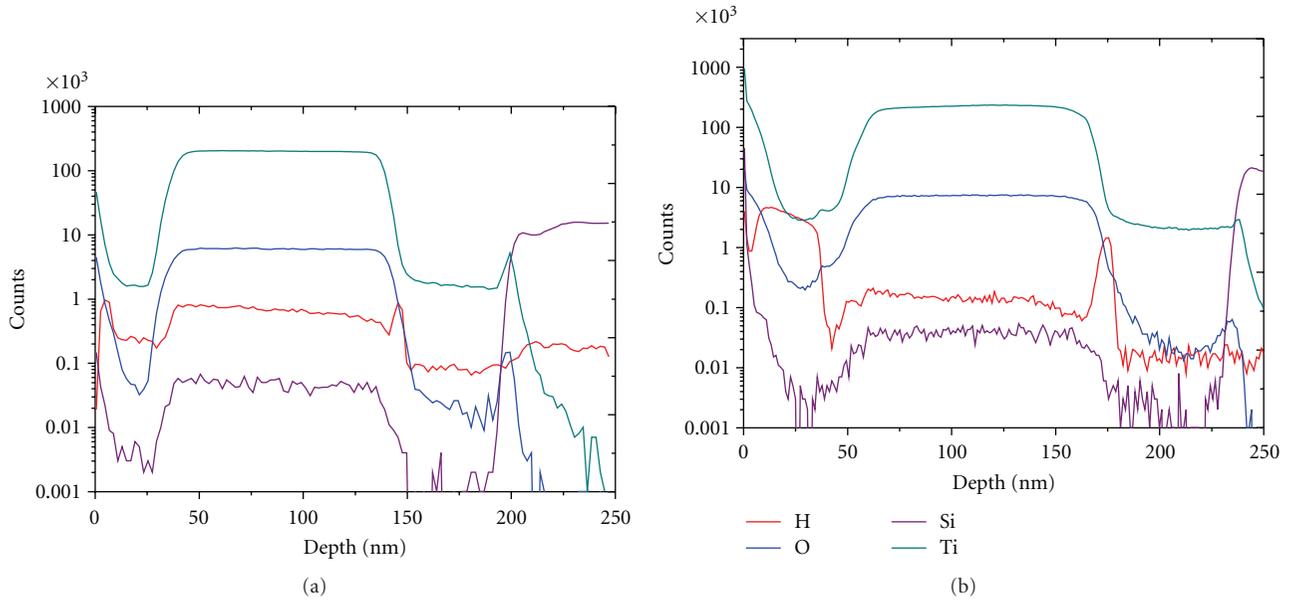


FIGURE 7: SIMS profiles for the sample Ti/TiO₂/Ti/Si before (a) and after (b) hydrogen charging.

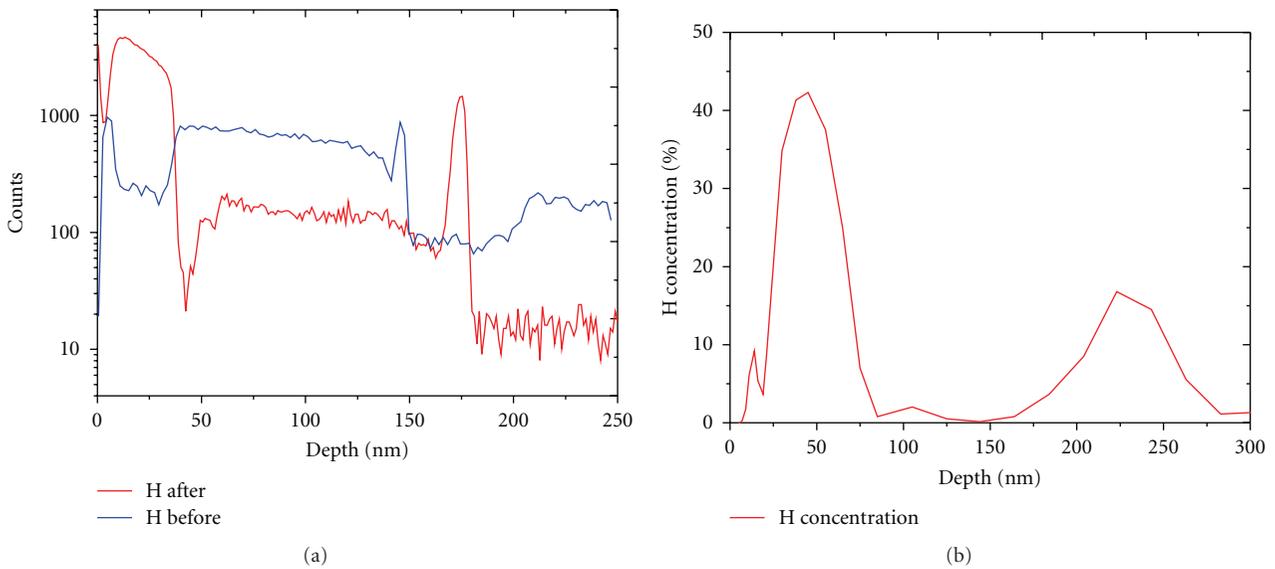


FIGURE 8: Hydrogen profiles for the sample Ti/TiO₂/Ti/Si measured by SIMS (a) and by N-15 (b).

Materials Science, Technische Universität Darmstadt) for his assistance at resistivity measurements and M. Perzanowski (Institute for Nuclear Physics, Polish Academy of Sciences) for preparing the palladium cover layers.

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