Topography and nanomechanical properties of Pd-C films

Research Article

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Abstract:

Atomic force microscopy (AFM) topographical studies and results of nanoindentation experiment for several palladium-carbon films (Pd-C film) deposited on various substrates and with varying palladium content are presented. Pd-C films were prepared by a physical vapor decomposition (PVD) process and next were modified by a chemical vapor decomposition (CVD) method to obtain carbonaceous porous structure with dispersed palladium nanograins and a variation in roughness.

The dependence of film topography on the kind of substrate such as Al_2O_3 , Mo polycrystalline foil and fused silica was studied by AFM. Nanomechanical properties such as hardness and the reduced indentation modulus were determined by nanoindentation. A comparison of these values for films with different Pd content deposited on various substrates is presented.

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1. Introduction

Nanostructural carbonaceous films containing nanograins of palladium are interesting because of their possible implementation in hydrogen applications and hydrogen compounds sensors. Because of the potential application of such films in various kinds of sensors, it is important to know their mechanical properties. Nanostructural carbonaceous films containing Pd nanograins can be applied as an active material for gas sensors and in nanoelec-

tronic systems (NEMS) [1, 2]. Such systems can also be applied as a chemiresistor type micro hydrogen gas, a nanomechanical sensor in liquids or as a nanomechanical sensor of temperature changes (via heat capacity measurements). In all these applications mechanical properties are important because these properties are changed in the effective sensing process (i.e. temperature, structural and chemical composition changes are connected to the existence of the sensing factor). AFM and the nanoindentation method are the most powerful instruments to study such changes in micro- and nanomechanical properties. For example, topography analysis and studies of topography changes due to a strain formation are con-

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nected to palladium hydride formation [3].

Nanostructural films composed of palladium and carbon are new materials with unique characteristics and structure in comparison with bulk Pd and carbonaceous macro-materials. Characterization of the nanomechanical properties such as nanohardness and the reduced modulus of new nanomaterials is particularly interesting because of their innovative application options. Even a small change of composition or form of nanomaterials affects their properties due to a change of material structure, morphology and surface topography. Additionally superficial and near surface properties have a huge impact on all material character because of a big surface to volume ratio.

We present results of studies of palladium-carbon films (Pd-C films) obtained on various substrates. The nanomechanical properties of such films were studied with the nanoindentation method, the technique designed to measure the mechanical properties of materials on the nanoscale. [4, 5]. We found that mechanical properties of Pd-C films depend on the content of palladium initially introduced and also depend on the structure and the topography of these films.

2. Experimental

2.1. Sample preparation

Pd-C films were obtained by a two step PVD/CVD method [6]. The PVD (physical vapor deposition) process was performed in a dynamic vacuum of 10^{-5} mbar from two separated sources. One source contained fullerenes C_{60} the other Pd acetate. Films were prepared on different substrates. The first set of samples were deposited on Al_2O_3 (S1-PVD) and molybdenum substrate, the second set on fused silica (S2-PVD). Depending on parameters of the technological process (current intensity through sources, sources-substrate distance and deposition time) samples with various Pd content were obtained (Tab. 1). In the second step this film was modified in CVD (Chemical Vapor Deposition) process at a temperature of $650^\circ C$ in the atmosphere of a xylene flow. We denote the S1-PVD sample modified in CVD process as S1-CVD and respectively the S2-PVD sample as S2-CVD.

Table 1. List of the samples studied.

Sample nr	Substrate	Pd content [wt %]
S1 PVD-a	Al_2O_3	~ 20
S1 PVD-m	Mo	~ 20
S2 PVD	Fused silica	~ 44

The relief of the film obtained on the Al_2O_3 substrate does not allow for an exact determination of the film thickness. The changes in the z -direction in surface height can reach $5 \mu m$ locally. The thickness of the film obtained on fused silica and Mo foil was ~ 300 nm. We suppose that for films obtained on different substrates under the same conditions their thickness might be similar. We used such substrates because of further application of these films as active layers in high temperature detectors. The Mo substrate was applied to obtain a flat surface for AFM imaging which deteriorates when applied in the detector because of high stress arising in the Mo foil during annealing. Films obtained on Al_2O_3 substrate are used as active layers in the detector in practice.

From the previous measurements – TEM, XRD [7] we know that films obtained in the PVD process are composed of Pd *fcc* type nanocrystals embedded in a matrix composed of a mixture of fullerene, graphite and amorphous carbon. Due to the CVD process, the carbonaceous matrix becomes porous and Pd nanocrystals agglomerated into big grains ($10 - 100$ nm). Additionally, due to CVD modification, Pd nanograins were also enclosed in graphite shells [7].

3. The nanoindentation technique

Nanoindentation was used to study the mechanical properties of the Pd-C films. All experiments were performed with a tip made of diamond with a shape of a 90° cube corner three-sided pyramid using a HYSITRON Tribo-scope attached to a scanning force microscope. From the load-displacement curve, mechanical properties including the reduced modulus E_r and the hardness H can be determined based on data analysis and the standard Oliver-Pharr approach [8]. The experiment was carried out under ambient pressure.

The hardness, defined by the ratio of the applied load to the area of the projection is determined using the formula:

$$NH = \frac{F_{\max}}{A_c(h_c)},$$

where $F_{\max}$ is the maximum applied load and A_c is the cross-sectional area corresponding to the contact depth h_c

$$A_c(h_c) = a_0 \cdot h^2 + a_1 \cdot h + a_2 \cdot h^{\frac{1}{2}} + a_3 \cdot h^{\frac{1}{4}} + a_4 \cdot h^{\frac{1}{8}} + a_5 \cdot h^{\frac{1}{16}}.$$

The reduced modulus E_r is a measure of the elastic properties of the tip-sample system and can be calculated from the load-depth curves according to the formula:

$$E_r = \frac{1}{2} \sqrt{\frac{\pi}{A_c(h_c)}} \frac{dF}{dh}.$$

The indents were performed either with a single trapezoid shape and multi-cycling load function with incremental load on the same local position [9]. Most indents were made with a peak load of 1 mN, but there were also measurements with peak loads of 500 μ N and more than 1 mN. Multi-cycling was used to generate a larger amount of measuring points to determine hardness and the elastic modulus and to check retarding processes during unloading in the material. In the latter typical hysteresis loops were visible. Such loops are characteristic of polymeric materials and represent visco-elastic material behavior. Since carbon is present in the films, this property could be interesting in describing the film and its mechanical response during the deformation process.

4. Result of AFM and nanoindentation

4.1. S1-PVD sample

Due to the large roughness of the sample deposited on Al_2O_3 (S1-PVD-a) AFM imaging could not be obtained. Therefore we used a sample obtained on Mo (S1-PVD-m) in the same technological process. The AFM image of S1-PVD sample (Fig. 1) shows a surface covered with hill-like grains of different shapes and height. The cross-line analysis performed with AFM in contact mode show that the roughness of the samples is ~ 28 nm.

Figure 1. AFM image of S1-PVD-m sample on Mo substrate with cross-line analysis (scan area $5 \mu\text{m} \times 5 \mu\text{m}$).

In Fig. 2 a typical load-displacement curve of nanoindentation measurements for the S1-PVD-a sample is presented. The elasto-plastic displacement of the sample under the influence of the indenter into the layer was generated. This type of displacement reflects in the load-displacement curve a change in a slope of the tangent of the unloading curve. If this slope was perpendicular to "depth" axis it would mean that it is ideal plastic displace-

Figure 2. Load-displacement curves for nanoindentation into the S1-PVD-a sample in different places.

a

b

Figure 3. Depth dependent (a) hardness (b) reduced modulus for S1-PVD sample.

ment. Measurements were performed in 4-cycling mode. In the first cycle an elastic reaction of the material was seen while in further cycles the reaction to a bigger loading force was more elasto-plastic. The evidence of such reactions is a slope of the relative loops. In subsequent cycles, there were no changes in the nature of the curve with depth. There are neither pop-ins nor hysteresis.

The indentation was mainly performed on these large hill-like grains. The hardness varies between 9 GPa and 16 GPa and the modulus values are between 80 GPa and 115 GPa. Some softer material was found between the grains (hardness less than 2 GPa and modulus 10 – 15 GPa). These lower values for H and E_r could be connected to a slip of the tip at the grain boundary. In Fig. 3 values of hardness and reduced modulus by the indent close to a grain boundary are denoted with * symbols. H decreases drastically from 12 GPa to 7 GPa, whereas the modulus remains at ~ 100 GPa. There are no hysteresis loops. Thus, the PVD deposited films seem to consist mainly of hard grains on the surface.

4.2. S1-CVD sample

In Fig. 4 AFM image presents the topography of the surface for the S1-CVD sample. The topography of this sample is different from the topography of the S1-PVD sample. It is found that the surface of the S1-CVD sample consists of grains with a diameter of about 50 – 150 nm. The roughness of the film is ~ 20 nm.

Figure 4. AFM image of S1-CVD sample on Al_2O_3 substrate with cross-line analysis (scan area $5 \mu\text{m} \times 5 \mu\text{m}$).

The load-displacement curves for the S1-CVD sample (Fig. 5) clearly show two different characteristic fingerprint curves which represent the heterogeneous composition of the Pd carbonaceous film. Most indented places have a loading curve with a shallow part at the beginning followed by a steep one. Additionally, pop-ins and hysteresis loops are observed. At a few places a low

penetration depth is obtained which is typical for hard particles. The hysteresis loops probably characterize the visco-elastic behavior of the carbonaceous matrix. For the nanocomposite materials visco-elastic behavior is observed during multi-cycling indentation when hysteresis appears. This is generally found in polymer materials. Due to the carbon/fullerene content in our samples such a behavior is also observed in the Pd-carbon samples. However the Pd-C samples show mainly typical plastic deformation which is characteristic for metals.

Smaller loops may indicate the influence of harder particles close to the indentation location. Large pop-ins could reflect the slip down the tip along harder grains. Large loops are often correlated with very small pop-ins, which could mean mainly carbonaceous material. The harder grains do not show loops, but sometimes two different slopes of the loading curve.

Figure 5. Load-displacement curves for nanoindentation into S1-CVD sample in different places.

The different load-displacement charts are reflected in two hardness and indentation modulus values (Fig. 6). Hard particles have a hardness of 4–14 GPa with a modulus of 60–125 GPa. The softer matrix has a hardness of 0.3–1 GPa with reduced moduli of 5–30 GPa.

Figure 6. Depth dependent (a) hardness (b) reduced modulus for S1-CVD sample.

4.3. S2-PVD sample

The S2-PVD film was deposited on a very smooth surface. The AFM image (Fig. 7) shows a smooth surface covered with small grains. The content of palladium in this film is more than 2 times higher than in the S1-PVD.

The load-displacement curves for the S2-PVD film show large pop-ins (Fig. 8). A pop-in marks the sudden transition between granular area and layer that could contain more soft material such as carbon. The pop-in starts at a

Figure 7. AFM image of S2-PVD sample on fused silica substrate with cross-line analysis (scan area 5 μm × 5 μm).

Figure 8. Load-displacement curves for nanoindentation into S2-PVD sample in different places.

penetration depth of ~ 58 nm.

The S2-PVD film does not show such a distribution as in the case of the S1-PVD/-CVD material, which is charac-

a

b

Figure 9. Depth dependent (a) hardness (b) reduced modulus for S2-PVD sample.

teristic of two different kinds of compounds. The hardness for the S2-PVD sample is between 0.6 – 1 GPa and the reduced modulus 18 – 27 GPa, respectively (Fig. 9).

4.4. S2-CVD sample

The AFM image shown in Fig. 10 presents the surface of the S2-PVD film modified in the CVD process. It can be seen that there are three types of objects on this surface: 1) long rods (length $\sim 4 \mu\text{m}$); 2) spherical small grains (diameter $\sim 30 - 50 \text{ nm}$); 3) very small grits-like objects (diameter few nm).

The shape of the load-depth curve (Fig. 11) shows an elastic-plastic character of the S2-CVD sample. The hysteresis for this curve is observed and it is much stronger

Figure 10. AFM image of S2-CVD sample on fused silica substrate with cross-line analysis (scan area $5 \mu\text{m} \times 5 \mu\text{m}$).

Figure 11. Load-displacement curves for nanoindentation into S2-CVD sample in different places.

than for the S1-CVD sample.

The nanoindentation measurements show differences in hardness and reduced modulus of S2-CVD film in comparison to the PVD process. Hardness is 0.1 – 0.18 GPa, and the reduced modulus of elasticity is 2 – 2.5 GPa. The hardness and indentation modulus is much smaller compared with those for the S2-PVD. This effect could be connected to a modification of carbon matrix in the CVD process to nanoporous form [6]. These results could also confirm the homogenous character of the deposited film.

5. Conclusion

- Films obtained in a single PVD process and those after an additional modification by the CVD process have different mechanical properties. These first

Figure 12. Depth dependent (a) hardness (b) reduced modulus for S2-CVD sample.

films consists of two different kinds of compounds with different mechanical properties.

- S1 film modified by CVD method has a superficial layer with higher hardness than the rest of the film which can be connected to a distribution of palladium grains only on the film surface. We have stud-

ied nanomechanical properties of fullerenes and we found that its shape of load-displacement curve has mostly plastic character and the hardness and reduced Young modulus are much lower than respective values for the observed carbonaceous palladium films [10].

- S2 films modified by CVD method are homogenous and are composed of soft material (probably carbon), which suggests that palladium in the form of very small grains is dispersed within the film volume and it does not have an impact on the hardness of the sample.

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References

- [1] X.M.H. Huang, M. Manolidis, Seong Chan Jun, J. Hone, *Appl. Phys. Lett.* 86, 143104 (2005)
- [2] S.E. Lyshevski, *Nano- and micro-electromechanical systems: fundamentals of nano- and micro engineering* (CRC Press, Boca Raton, FL, 2005)
- [3] R. Duś, E. Nowicka, R. Nowakowski, *Acta Phys. Pol. A* 114, 29 (2008)
- [4] G. Timp, *Nanotechnology* (Springer, New York, 1999)
- [5] A.C. Fischer-Cripps, *Nanoindentation* (Springer-Verlag, New York, 2002)
- [6] E. Czerwosz et al., *Vacuum* 82, 372 (2008)
- [7] M. Kozłowski et al., *Journal of Achievements in Materials and Manufacturing Engineering* 37, 304 (2009)
- [8] W.C. Oliver, G.M. Pharr, *J. Mater. Res.* 7, 1564 (1992)
- [9] B. Wolf, A. Richter, *New Journal of Physics* 5, 15.1 (2003)
- [10] A. Richter, R. Ries, R. Smith, M. Henkel, B. Wolf, *Diam. Relat. Mater.* 9, 170 (2000)