RHEED AND EELS INVESTIGATION OF Pd/Al BIMETALLIC SYSTEM

V.Moroz, V.Matolín, K.Mašek

Department of Electronics and Vacuum Physics, Faculty of Mathematics and Physics, Charles University, V Holešovickách 2, 180 00 Prague 8, Czech Republic
e-mail: moroz@mbox.troja.mff.cuni.cz

Pd/Al alloys have very interesting properties from the point of view of their possible application in heterogeneous catalysis. Preparation of small heteroepitaxial Pd/Al alloy particles opens a new way in studies of the influence of Pd/Al crystallographic structure on the alloy catalytic properties. Pd/Al alloy particles were grown by molecular beam epitaxy method. Their crystallographical structure was controlled by reflection high energy electron diffraction (RHEED). It was found that Pd deposited on epitaxial 3-D Al particles grown on KCl is intermixing with Al. This process is accompanied by the variation of lattice parameter from the Al value to the Pd one. The electron energy loss spectroscopy (EELS) was used as an auxiliary method for chemical analysis.

1. Introduction

In the recent years, a great effort has been made to investigate the structural, electronic and chemical properties of bimetallic systems. It is well known that a bimetallic surface can exhibit chemical and catalytic properties that are very different from those of the individual metals.

The main interest of this work was to investigate the formation of supported Pd/Al bimetallic system. Bimetallic bonding can induced significant changes in the band structure of a metal, introducing in this way the possibility for new and unique chemical properties. Due to a very strong Al - Pd interaction [1-3] new bimetallic catalysts based on the Pd/Al alloy can be developed. We have prepared the supported single-crystalline model of bimetallic catalyst to study its formation during the early stages of the growth. We investigated the structure and epitaxial parameters and the evolution of lattice parameter during the growth by RHEED (reflection high electron energy diffraction). The precise measurement using so-called subpixel detection method [4] showed the changes of lattice parameter depending on mutual concentration of the Pd and Al atoms in the alloy.

The chemical analysis was performed by means of EELS (electron energy loss spectroscopy) which is very sensitive to the changes on the sample surface. The surface cleanliness was checked by the AES (Auger electron spectroscopy).

2. Experimental procedures

The studies were performed in a special designed UHV system. The EELS spectra were obtained with a cylindrical mirror energy electron analyzer. During the measurements the primary electron energy was set to 300 eV. The EELS peaks were measured in direct mode.

The chamber was also equipped with RHEED facility operated at the accelerating voltage of 40 kV. The diffraction pattern was recorded by a RHEED - Vision Computer System. A special software equipment permitted to obtain the position of diffraction spots with very high precision [4] and in this way to evaluate the lattice parameters of the deposit. The RHEED diffraction pattern development was recorded in real time using a video recorder. It permitted to treat the diffraction pattern later in order to analyze the particle lattice parameter values as a function of the deposition time.

The Al and Pd metals were deposited using a special evaporation cell - MEBES (Micro Electron Beam Evaporation Source [5]) operating at very low evaporation rate (several monolayers per minute). The deposition was carried out at a background pressure about $5x10^{-7}$ Pa and at substrate temperature of 470 K. A liquid nitrogen cooled cryopanel, surrounding the MEBES cell, kept the stable pressure conditions during the deposition.

The (001) KCl single-crystal substrate surface was prepared by cleaving in air. The substrate was immediately introduced into the preparation chamber and heated before the deposition during 30 min at the temperature of 770 K under UHV conditions.

The sample was prepared at a substrate temperature of 470 K during the deposition. Firstly, the Al epitaxial layer was prepared (during 10 min) and then Pd was deposited (during 15 min) on the Al/KCl system. By this way the Pd/Al/KCl epitaxial system was obtained. The simultaneous deposition of Pd and Al metals produced non-oriented Pd/Al layer [6].

3. Results

The resulting diffraction pattern from the Pd/Al bimetallic system is presented in Fig. 1. The spot like form of diffraction pattern shows the three-dimensional growth of particles. The elongated spots correspond to the diffraction from the flat substrate surface having only the terraces of monoatomic height as it is obviously expected in the case of the cleaved single-crystals. The presence of diffraction spots from the substrate confirms non-continuous form of the Pd/Al layer. The similar diffraction pattern was observed after the deposition of Al (presented elsewhere [6]). The interpretation of diffraction pattern gives the following mutual orientation between the substrate and deposited metal lattices:

Pd/Al (001) // KCl (001)

Pd/Al [100] // KCl [100].

During the Pd deposition, the presence of two sets of diffraction spots corresponding to the separate populations of Pd and Al particles was not observed. From this fact we can conclude that the layer consists of one particle population formed by Pd/Al alloy. It is in agreement with results in Ref. 1 and 3 where the Pd was grown on bulk Al substrate.

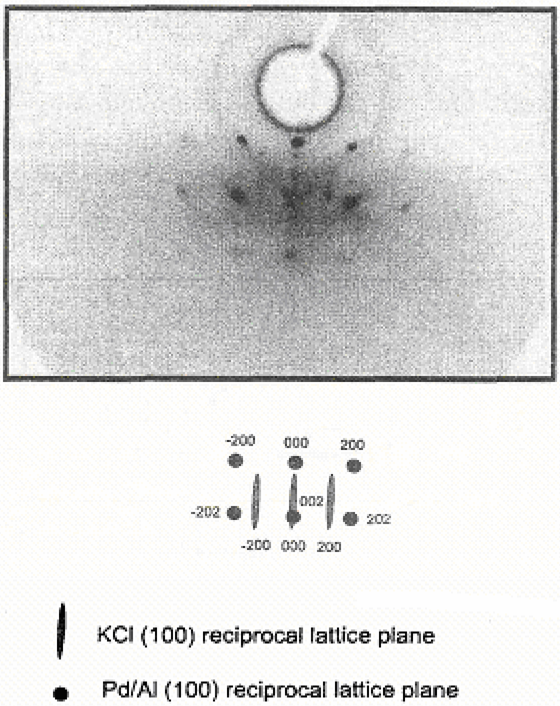

Fig. 1. The RHEED diffraction pattern and its interpretation of Pd/Al epitaxial bimetallic system on (001) KCl substrate. The primary electron beam is parallel to the [100] KCl crystallographic direction.

The ex-situ XPS analysis gave the relative average concentration of Al/Pd = 1.1 after the deposition process [6]. According to this calculated value one can estimate the relative concentration during the deposition of Pd.

The precise measurement of deposit diffraction spot distances permitted to determine the deposit lattice parameter value *a* in directions parallel and perpendicular to the substrate surface, respectively. The both are plotted in Fig. 2. We can see that the *a*-parallel kept the constant value during the growth of Al particles. At the time of 600 s the Al deposition process was stopped and Pd deposition was started at 780 s. The dramatic change of lattice parameter was observed in the range from 1000 s to 1300 s. For this range the estimate of relative Al/Pd concentration changes were found from 4 (at 1000 s) to 1.8 (at 1300 s). After this range the lattice parameter which corresponded to the slightly contracted Al lattice spacing (bulk value 4.04 Å) was changed to the value corresponding to the Pd (also slightly contracted in comparison with the bulk value of Pd 3.89 Å). No any changes of diffuse background intensity were observed. One can conclude that the bimetallic system stays in the crystalline form also when the lattice parameter is change from one value to another.

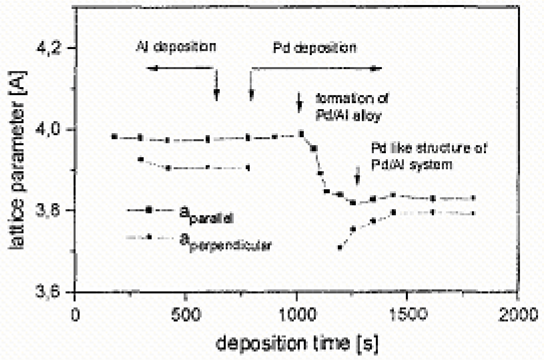

Fig. 2. The evolution of the lattice parameter value of Al and/or Pd/Al alloy particles in directions parallel (∝) and perpendicular (≥) to the (001) KCl substrate surface during the growth.

The EELS spectra were recorded after each step of experiment – Al and Pd depositions. The spectra were taken at a primary electron beam energy of 300 eV. The inelastic background was moved using the Tougaard's method [7] to obtain the exact form of EELS spectra. The results after the subtraction of the elastic peak and the inelastic background are presented in the Fig. 3 for both Al/KCl and Pd/Al/KCl systems, respectively. After the Pd deposition on Al/KCl system the shape of loss spectrum changed due to the different excitation energies of plasmons for Al and Pd. The Al energy loss spectrum (a) displays maxima at 11 eV and 17 eV while the Pd spectrum (b) exhibits characteristic losses at 7 eV, 12 eV and 23 eV. One can deduce that the peak at 11,5 eV is composed of characteristic losses of both Al and Pd metals. The broad peak at higher energy corresponds to the set of convoluted characteristic losses from KCl substrate. The fact that the signal from KCl substrate is still observable after the both depositions confirms the results of RHEED observations: the Al-Pd deposit formed the non-continuous layer composed of three-dimensional particle alloy.

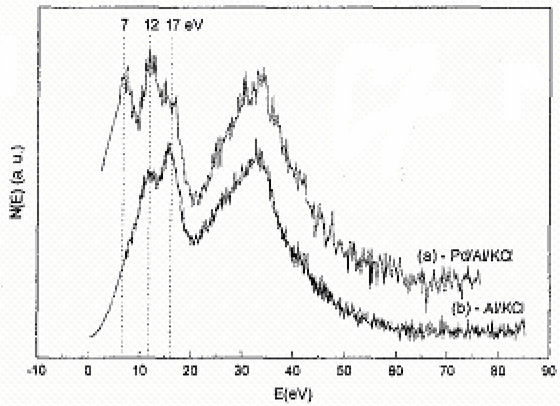

Fig. 3: Electron energy loss spectra of Al/KCl (a) and Pd/Al/KCl (b) systems. The primary electron beam energy was set to 300 eV.

4. Conclusions

The orientated Pd/Al alloy particles were observed in the case of Al layer growth followed by the Pd deposition. The changes of lattice parameter were found in the range of relative Al/Pd concentration between the values of 4 and 1.8. For higher concentration of Pd the alloy had FCC Pd-like crystal structure.

The results showed that it is possible to prepare heteroepitaxial Pd/Al particles. It permits to investigate the structure and electronic properties of bimetallic Pd/Al catalysts. The EELS method can be used as an auxiliary technique for the investigation of the chemical composition of such systems.

Acknowledgments

This work was supported by grants Nos. 202/97/P077 and 202/99/1714 of the Czech Grant Agency and by grant No. VS 97116 of the Ministry of Education, Youth and Sports.

References

1. L.Q.Jiang, M.W.Ruckman, M.Strongin, *Phys. Rev. B* **39,** 1564 (1989).
2. B.Frick, K.Jacobi, *Phys. Rev. B* **37**, 4408 (1988).
3. V.Shutthanandan, A.A.Saleh, N.R.Shivaparan, R.J.Smith, *Surf. Sci.* **350**, 11 (1996).
4. V.Matolín, B.Peuchot, *Thin. Sol. Films* **259**, 65 (1995).
5. V.Nehasil, K.Mašek, O.Moreau, V.Matolín, *Czech J. Phys*., **47**, 261 (1997).
6. K.Mašek, V.Moroz, V.Matolín, *Surface Review and Letters* **6**, 825 (1999).
7. S.Tougaard, *Surf. and Interface Anal.*, **115**, 453 (1988).

ДОСЛІДЖЕННЯ БІМЕТАЛІЧНИХ СИСТЕМ Pd/Al МЕТОДАМИ ДИФРАКЦІЇ ВІДБИТИХ ВИСОКОЕНЕРГЕТИЧНИХ ЕЛЕКТРОНІВ ТА СПЕКТРОСКОПІЇ ЕНЕРГЕТИЧНИХ ВТРАТ ЕЛЕКТРОНІВ

В.Мороз, , В.Матолін, К.Машек

Кафедра електроніки і вакуумної фізики, Математико-фізичний факультет,
Карлів університет, Прага, Чехія
e-mail: moroz@mbox.troja.mff.cuni.cz

Сплави Pd/Al мають дуже цікаві властивості з огляду на можливе їх використання в гетерогенному каталізі. Приготування малих гетероепітаксіальних частинок сплавів Pd/Al відкриває нові шляхи у вивченні впливу кристалографічної будови Pd/Al на каталітичні властивості сплаву. Частинки сплаву Pd/Al було вирощено методом молекулярно-пучкової епітаксії. Їхня кристалографічна структура контролювалася дифракцією відбитих високоенергетичних електронів. Виявлено, що Pd, осаджений на епітаксіальні тривимірні частинки Al, вирощеного на KCl, змішується з Al. Цей процес супроводжується зміною параметра гратки від значення, характерного для Al, до величини, характерної для Pd. Як додатковий метод хімічного аналізу використовувалася спектроскопія енергетичних втрат електронів.