

Gas Sensing Properties of SnO₂ Thin Films Modified by Ag Nanoclusters Synthesized by SILD Method

G. Korotcenkov, B.K. Cho, L.B. Gulina, and V.P. Tolstoy

Abstract—The effect of SnO₂ surface modification by Ag nanoclusters, synthesized by SILD method, on the operating characteristics of thin film gas sensors was studied and models for the promotional role of Ag additives were discussed. It was found that mentioned above approach can be used for improvement both the sensitivity and the rate of response of the SnO₂-based gas sensors to CO and H₂. At the same time, the presence of the Ag clusters on the surface of SnO₂ depressed the sensor response to ozone.

Keywords—Ag nanoparticles; deposition; characterization; gas sensors; optimization

I. INTRODUCTION

NANOCCLUSERS of Ag are objects for intensive research in the field of catalysis, Si porosification, and design of both chemical sensors and biosensors [1]-[4]. For gas sensor applications, the most important effects of surface modification by Ag nanoclusters are the increase both sensitivity and selectivity of sensor response to specific analytes, such as H₂ and H₂S [2], [5].

For the Ag cluster synthesis and deposition, different methods such as impregnation, spray pyrolysis deposition, thermal evaporation, chemical vapor deposition, laser ablation, electroless plating, magnetron sputtering, chemical deposition and some other have already been demonstrated [4], [6], [7]. In this report we present results related to Ag clusters synthesis by Successive Ionic Layer Deposition (SILD) method.

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Detailed description of SILD method one can find in [8], [9]. Deposition of Ag nanoclusters was used for surface functionalizing of the SnO₂ films aimed for gas sensor design.

II. EXPERIMENTAL DETAILS

For the Ag⁰ nanolayers synthesis by SILD method the reaction of silver cations reduction in weakly-alkaline solutions of hydrogen peroxide was chosen [10].

The synthesis of Ag on the substrates by SILD was carried out using the following route. During the first SILD cycle substrates used were treated in a metal salt solution (0.01M solution of Ag(NH₃)₂NO₃) and then samples were washed with distilled water to remove the non-reacted reagents, treated with reductant, and again washed in distilled water. A 0.1 M solution of ascorbic acid or a 0.3 M solution of H₂O₂(OH⁻) (both were supplied by Vekton) were used as reductants. The concentrations of solutions used were selected basing on the previous experience. Time of processing with the Ag solution and time of the subsequent washing with water were 30 sec each. Time of processing with the reductant solution and time of the subsequent washing with water were 1 min each. Such treatments represented the first deposition cycle.

At the following cycles of deposition at the stage of Ag⁺ adsorption solutions such as Ag(NH₃)₂NO₃ or AgNO₃ were used. The first route was similar to the one described earlier. The second route included a consistent treatment in the solutions AgNO₃, H₂O, ascorbic acid and H₂O. Parameters of the hydrogen peroxide treatment and washing were kept unchanged. For Ag deposition we have been using from 1 to 10 cycles.

The SnO₂ layers deposited by spray pyrolysis method were used for surface modification [11]. The thickness of the layers was 40-50 nm. The SnO₂ layers were nano-scaled with averaged grain sizes ranging from 15 to 25 nm [12]. The gas sensing characteristics were tested in steady state and transient modes using a flow type reactor. For mentioned above experiments measurement cycle air → testing gas → air was used. Air mixtures containing reducing gases CO or H₂ (1000 ppm), and oxidizing gas ozone (~1 ppm) were used as testing analyte. Sensor response was calculated as both the ratio R(gas)/R(air) for gas containing ozone, and the ratio R(air)/R(gas) for gas containing CO or H₂. Response and recovery times were estimated at the level of 90% (τ_{0.9}) and 50% (τ_{0.5}) of the steady state value of the film conductivity, respectively. Before gas sensing properties measurements,

sensors were annealed at 500 °C during 30 min for their stabilization

III. RESULTS AND DISCUSSIONS

A. Ag Nanocluster Characterization

Analysis of the SEM image of silver particles deposited by using the silver ammoniate and H₂O₂ solutions has shown that the averaged particle's size is up to 1 μm and they agglomerate the 100–200 nm particles. When the silver nitrate and ascorbic acid solutions were used as reagents, the size of deposited Ag nanoparticles was 20–30 nm.

However, one should note that a detailed study of the formed layer morphology, made by using AFM microscopy (see Fig. 1), has shown that even in case of the Ag nanolayer forming with using Ag(NH₃)₂NO₃ and H₂O₂ solutions, at the surface, besides big particles, nanoclusters are being formed. They are distributed along the square uniformly, and in the dependence of technological route have sizes ranged from 1-5 nm to 50 – 100 nm. The size of those clusters increases with the increasing of the deposition cycles number.

The results of more detailed characterization of Ag nanoclusters, synthesized by SILD method on the surface of Si substrates and discussions of their growth mechanism one can find in [13].

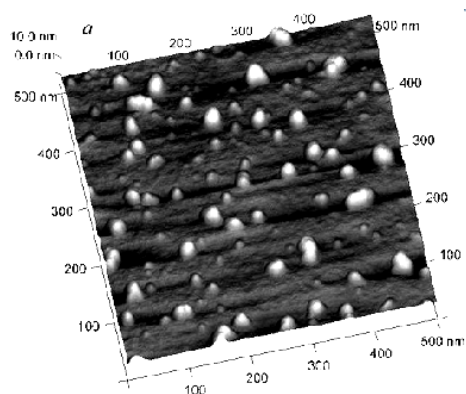


Fig. 1 AFM images of the Ag⁰ nanoparticles synthesized on a silicon surface by 2 SILD cycles using solutions AgNO₃ and ascorbic acid

B. Gas sensing characteristics

The results of the influence of surface modifications by Ag on the gas sensing characteristics of the SnO₂-based gas sensors are shown in Figs. 2 and 3. It is seen that Ag deposition on the SnO₂ surface promotes the increase of sensor response to reducing gases by more than 5- 10 times. This demonstrates that this method of surface modification based on the SILD technology can be used for improvement of the SnO₂-based gas sensor's parameters. At that, an optimizing effect of the surface modification by Ag clusters is observed in a broad range of surface coverage. For Pd doping we observed strong maximum at certain surface concentration of Pd nanoclusters [14]. Mentioned above feature of SnO₂-Ag

sensors can be considered as an advantage of the surface modification by Ag clusters using SILD technology

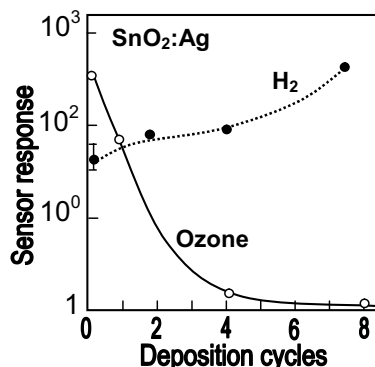


Fig. 2 Influence of the surface modification by Ag nanoclusters on the SnO₂-based sensor response to H₂ and ozone: H₂ - T_{oper}= 425 °C; ozone - T_{oper}= 275 °C

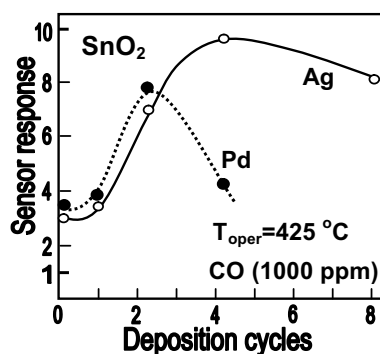


Fig. 3 Influence of SnO₂ surface modification on sensor response to CO

It is important that maximum responses of the SnO₂-based gas sensors to H₂ and CO were achieved at different Ag coverage. For CO detection, the maximum sensor response was observed after four cycles of Ag deposition (Fig. 3), while for H₂ detection even after 8 deposition cycles we observed the increase of sensor response (Fig. 2). This means that Ag clusters with the same size have different activity with different gases. The last one is normal for heterogeneous catalysts.

The surface modification by Ag also promotes the decrease of response time (see Fig. 4). However, this effect takes place only for sensors fabricated using small number of Ag deposition cycles. Unfortunately, the nature of this effect is strange and better understanding of this effect requires additional study.

The influence of the surface modification by Ag on sensor's response to ozone (see Fig. 2) is another interesting effect observed after surface modification by Ag. The presence of Ag additives on the SnO₂ surface sharply suppresses the sensor response to ozone. As one can see from Fig. 2, already after two deposition cycles the response to ozone decreases by more

than 100 times. This effect allows improving selectivity of the sensors of reducing gases, working in real conditions, when the appearance of ozone in atmosphere is possible. In this case Ag nano-layers act as a catalytically active filter for ozone. However, the nature of this effect is not understandable completely, because after 1-5 deposition cycles Ag does not form continuous layer.

C. Discussions

At present for explanation of gas sensitive properties of the SnO₂-based sensors modified by Ag it is usually being used electronic model suggested in refs. [3], [15]. This model is based on the change of the Ag oxidation state at the SnO₂ surface during interaction with gas detected, which is accompanied by the change of potential barrier at the Ag-SnO₂ interface

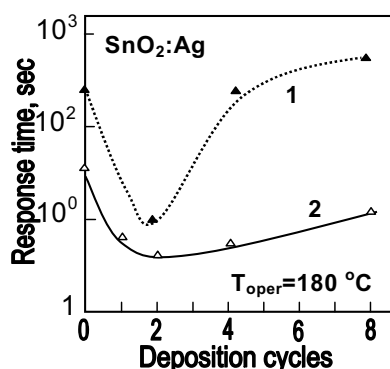


Fig. 4 Influence of the surface modification by Ag nanoclusters on response time of the SnO₂-based sensors: T_{oper} = 275 °C; 1- $\tau_{0.9}$ and 2- $\tau_{0.5}$.

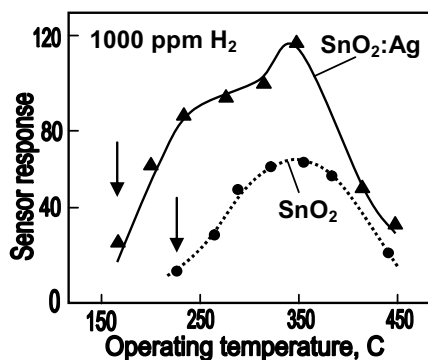


Fig. 5 Influence of SnO₂ surface modification on temperature dependencies of gas response to H₂

We agree with such approach, because our data obtained are in the frame of present model. In particular, the temperature range of sensitization (see Fig. 5) coincides with the temperature range, where the change of chemical composition of Ag clusters is possible [16]-[18].

The influence of operating temperature on the SnO₂ resistivity dependence from the number of deposition cycles

can also be considered as a confirmation of mentioned above model. The increase of resistivity of SnO₂ films modified by Ag is also being observed just in indicated earlier temperature range (T_{oper} < 400 °C). Observed behavior of the film resistance is in accordance with conclusion made by Matsushima et al. [36] that redox couple Ag⁺/Ag⁰ acts as a surface acceptor. At temperatures exceeding 400 °C the growth of SnO₂ resistivity is insignificant, or is absent (see Fig. 6, curve 3). All above mentioned testifies that the presence of Ag in oxide state really is required condition for the appearance of the optimizing effect in the SnO₂ sensors with Ag modified surface during detection of reducing gases.

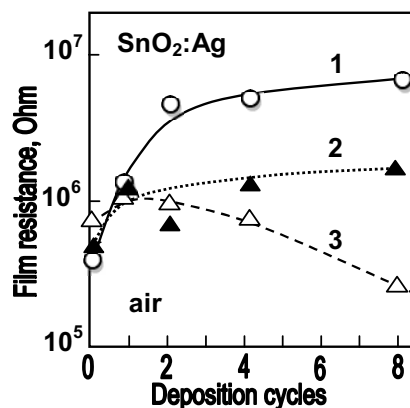


Fig. 6 Influence of surface modification by Ag nanoclusters on response and response time of SnO₂-based sensors: 1-T_{oper} = 225 °C; 2-275 °C; 3-425 °C

The presence of Ag₂O could also be the main reason of the increased activity of the Ag clusters to ozone. Research made in [19], [20] has shown that Ag₂O is effective heterogeneous catalyst for the decomposition of ozone. Just this fact can explain the decrease of sensitivity to ozone of SnO₂ sensors modified by Ag. Decomposition of ozone at Ag₂O nanoclusters can take place without electronic exchange with SnO₂, necessary for the sensor response appearance

IV. CONCLUSIONS

Conducted research has shown that the SILD technology is acceptable for the controllable forming of the Ag nanoparticles at the surface of different substrates including SnO₂ films deposited by spray pyrolysis. The size of the Ag nanoparticles deposited can be controlled by varying composition of solutions used and the number of the SILD cycles. As it was established, the size of the Ag nanoclusters depending on a synthesis conditions may vary from 1-5 nm to 500 nm. It was shown that surface modification of the SnO₂ films by the Ag nanoparticles deposited by SILD technology is also an effective method for the sensor parameters optimization. Modification by Ag promotes both the increase of sensor response of the SnO₂-based gas sensors to reducing gases, and the decrease of sensitivity to oxidizing gases (ozone). It testifies that the SnO₂:Ag sensors will be more selective to

reducing gases in comparison with sensors designed on the base of unmodified material. The last one is important for CO or H₂ sensors working in real environment containing ozone. SnO₂ modification by Ag nanoclusters is also being accompanied by the decrease of the response time.

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REFERENCES

- [1] O. M. Luo, X. Yuan, and X. Zheng, "Catalyst characterization and activity of Ag–Mn, Ag–Co and Ag–Ce composite oxides for oxidation of volatile organic compounds", *Appl. Catal. A*, vol. 175, pp. 121-129, 1998.
- [2] M.S. Tong, G.R. Dai, Y.D. Wu, and D.S. Gao, "High sensitivity and switching-like response behavior of SnO₂-Ag-SnO₂ element to H₂S at room temperature", *J. Mater. Sci.: Mater. Electron.*, vol. 11, pp. 661-665, 2000.
- [3] J. Zhang, and K. Colbow, "Surface silver clusters as oxidation catalysts on semiconductor gas sensors", *Sens. Actuators B*, vol. 40, pp. 47–52, 1997.
- [4] X. Li, and P.W. Bohn, "Metal-assisted chemical etching in HF/H₂O₂ produces porous silicon", *Appl. Phys. Lett.*, vol. 77, no. 16, pp. 2572-2574, 2000.
- [5] J. Li, Y. Wang, X. Gao, Q. Ma, L. Wang, and J. Han, "H₂S sensing properties of the SnO₂-based thin films", *Sens. Actuators B*, vol. 65, pp. 111–113, 2000.
- [6] Y. Song, K. Cui, L. Wang, and S. Chen, "The electrodeposition of Ag nanoparticles on a type I collagen-modified glassy carbon electrode and their applications as a hydrogen peroxide sensor", *Nanotechnology*, vol. 20, 105501, 2009.
- [7] T. Qiu, X.L. Wu, J.C. Shen, P. C. T. Ha, and P. K. Chu, "Analysis of the noble metal catalytic additives introduced by impregnation of as obtained SnO₂ sol–gel nanocrystals for gas sensors", *Nanotechnology*, vol. 17, pp. 5769-5772, 2006.
- [8] G. Korotcenkov, V. Tolstoy, and J. Schwank, "Successive ionic layer deposition (SILD) as a new sensor technology: synthesis and modification of metal oxides", *Meas. Sci. Technol.*, vol. 17, pp. 1861-1869, 2006.
- [9] V.P. Tolstoy, "The peroxide route of the successive layer deposition procedure for synthesizing nanolayers of metal oxides, hydroxides and peroxides", *Thin Solid Films*, vol. 307, pp. 10-13, 1997.
- [10] E. Janata, A. Henglein, and B.G. Ershov, "First Clusters of Ag⁺ ion reduction in aqueous solution", *J. Phys. Chem.*, vol. 98, pp. 10888–10890, 1994.
- [11] G. Korotcenkov, V. Brinzari, M. DiBattista, J. Schwank, and A. Vasiliev, "Peculiarities of SnO₂ thin film deposition by spray pyrolysis for gas sensor application", *Sens. Actuators B*, vol. 77, no. 1-2, pp. 244-252, 2001.
- [12] V. Brinzari, G. Korotcenkov, J. Schwank, V. Lantto, S. Saukko, and V. Golovanov, "Morphological rank of nano-scale tin dioxide films deposited by spray pyrolysis from SnCl₄.5H₂O water solution", *Thin Solid Films*, vol. 408, pp. 51-58, 2002.
- [13] L.B. Gulina, G. Korotcenkov, B.K. Cho, and V.P. Tolstoy, "Ag nanoclusters synthesized by SILD method", *J. Mater. Sci.*, in press, 2011.
- [14] G. Korotcenkov, V. Brinzari, Y. Boris, M. Ivanov, J. Schwank, and J. Morante, "Surface Pd doping influence on gas sensing characteristics of SnO₂ thin films deposited by spray pyrolysis", *Thin Solid Films*, vol. 436, no. 1, pp. 119-126, 2003.
- [15] S. Matsushima, Y. Teraoka, N. Miura, and N. Yamazoe, "Electronic interaction between metal additives and tin dioxide in tin dioxide-based gas sensors", *Jpn. J. Appl. Phys.*, vol. 27, pp. 1798-1802, 1988.
- [16] M.X. Yang, P.W. Jacobs, C. Yoon, L. Muray, E. Anderson, D. Attwood and G.A. Somorjai, "Thermal stability of uniform silver clusters prepared on oxidized silicon and aluminum surfaces by electron beam lithography in oxidizing and reducing ambient", *Catal. Lett.*, vol. 45, pp. 5-13, 1997.
- [17] J.F. Weaver, and G.B. Hoflund, "Surface characterization study of the thermal-decomposition of AgO", *J. Phys. Chem.*, vol. 98, no. 34, pp. 8519-8524, 1994.
- [18] G.B. Hoflund, Z. F. Hazos, and G.N. Salaita, "Surface characterization study of Ag, AgO, and Ag₂O using x-ray photoelectron spectroscopy and electron energy-loss spectroscopy", *Phys. Rev. B*, vol. 62, no. 16, pp. 11126-11133, 2000.
- [19] B. Dhandapani, and S.T. Oyama, "Gas phase ozone decomposition catalysts", *Appl. Catal. B*, vol. 11, pp. 129-166, 1997.
- [20] S. Imamura, M. Ikebata, T. Ito, and T. Ogita, "Decomposition of ozone on a silver catalyst", *Ind. Eng. Chem. Res.*, vol. 30, pp. 217-221, 1991.

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