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Fabrication of Nanoporous Platinum Films with Dealloying Method for Hydrogen Sensor Application †

Melike Sener [1], Ali Altuntepe [2], Recep Zan [2,3] and Necmettin Kilinc [1,*]

[1] Department of Physics, Faculty of Science & Arts, Inonu University, Malatya, Türkiye; mlksener44@gmail.com
[2] Nanotechnology Application and Research Center, Niğde Ömer Halisdemir University, Niğde, Türkiye; altuntepeali@gmail.com (A.A.); recepzan@gmail.com (R.Z.)
[3] Department of Physics, Faculty of Science & Arts, Niğde Ömer Halisdemir University, Niğde, Türkiye
* Correspondence: necmettinkilinc@gmail.com

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Abstract: In this research, nanoporous platinum film is synthesized by using the dealloying method Platinum-copper (Pt-Cu) alloy films with approximately 50nm are prepared on the glass by using the magnetron co-sputtering technique. In order to obtain nanoporous Pt, Pt-Cu alloy films are dealloyed in 1 M nitric acid solution for different times. It is observed that when dealloyed in the nitric acid solution for 5 h, Cu was completely removed from the alloy, and nanoporous Pt with a regular pore structure was obtained. The fabricated nanoporous Pt film is tested for hydrogen detection in the concentration range of 10 ppm—5% hydrogen at various temperatures. The results demonstrated that the sensitivity of nanoporous Pt is about 6.5 for exposure to 1% hydrogen, and the sensing mechanism of nanoporous Pt could be explained with the surface scattering phenomenon.

Keywords: platinum; nanoporous; resistive sensor; hydrogen sensor; co-sputtering; dealloying method

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1. Introduction

Hydrogen, an abundant element in the universe, is an efficient, clean, and a renewable future energy source. Hydrogen is also an industrial gas used in many areas such as chemistry (as a reducing medium in crude oil refining, plastics, flat glass industry, etc.), semiconductors (as process gas in thin film deposition and annealing atmospheres), food products (for oils and fats hydrogenation), and transportation (in cars, trains, fuel cells, and spacecraft) [1]. However, it is a gas with a lower explosion limit of 4% in air and a low ignition energy. Therefore, a slight gas leak can cause serious concern, and the use of hydrogen poses a severe safety concern. Hydrogen gas cannot be detected by the human senses, and is tasteless, colorless, and odorless. So, when hydrogen or hydrogen containing gases are used, the safety is an important parameter. Therefore, the development of hydrogen sensors is vital and this sensors should respond quickly, have a wide sensing range, and are capable of being deployed in city scale networks [2]. In addition, a lot of research is underway to continuously improve sensor parameters such as selectivity, sensitivity, reliability, and response time, as well as diminish cost, sensor size, and power consumption, to meet future demands for the use of hydrogen in technology [3].

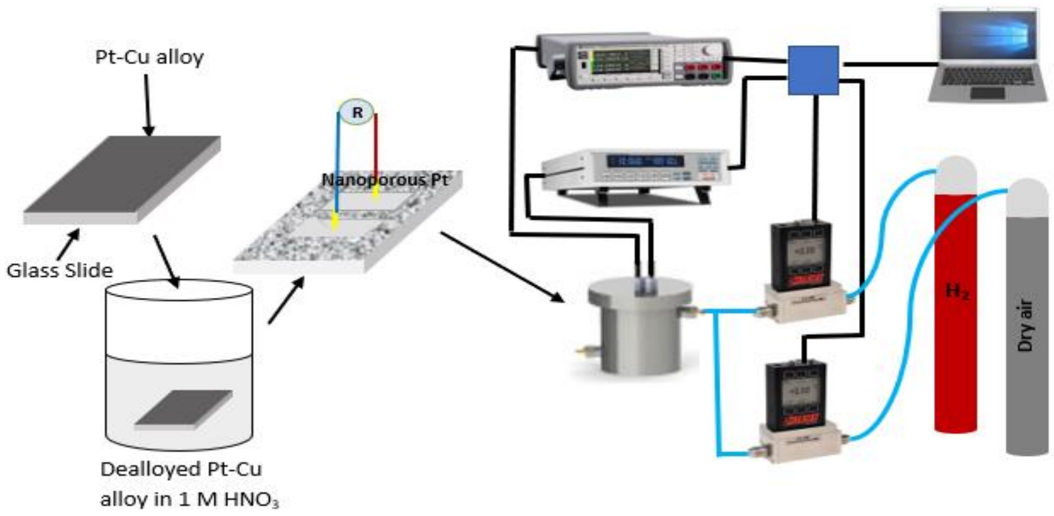
Metal and metal alloy nanomaterials, which have very good physical and chemical properties, have attracted great attention due to their important applications in various fields such as catalysis, battery, actuator, optics, sensors and medical therapy [4–6]. The performance of nanomaterials can be increased by adjusting parameters such as size, shape, morphology, composition and structure. Porous nanomaterials have superior physical properties such as very good geometric structure, large surface area, fine pores and stability [7–11]. Dealloying, one of the porous material production methods, is a corrosion process where the selective dissolution of an active component from a homogeneous, single-phase alloy consisting of bi- or multi-component metals with different chemical activities under suitable corrosion conditions leaves a porous residue behind [12,13]. The network architectures of dealloyed metals contain nanoscale struts and ligaments. Such a structural feature enhances the mechanical performance for their applications as functional or lightweight high-strength materials in sensing and actuating devices [14].

Platinum (Pt), which is one of the noble metals, makes these materials widely used in areas such as chemical, petrochemical, pharmaceutical, electronic and automotive industries, thanks to its very good resistance to corrosion and outstanding catalytic and electrical properties [10,11]. Pt, Pd and their alloys with other metals are used as sensing layer for resistive metallic hydrogen sensors [15]. They are also used as a sensing layer for optical, magnetic, mechanical hydrogen sensors, and as contact material for semiconductor resistive hydrogen sensors and work function based hydrogen sensors. Absorption of molecular hydrogen by Pd or Pt, changes in physical properties such as electrical, mass, volume and magnetic can be used to develop hydrogen sensors [16]. There are a few studies about Pt based resistive hydrogen sensor compared to Pd based resisitive hydrogen sensors.

In this report, nanoporous Pt films are fabricated by using dealloying method. The temperature and concentration dependent hydrogen gas sensing properties of these films are studied.

2. Materials and Methods

Platinum-copper (Pt-Cu) alloy films with approximately 50nm are coated on a microscope glass slide by using the magnetron co-sputtering method with an atomic ratio of 15:85, respectively. In order to obtain nanoporous Pt, Pt-Cu alloy films are dealloyed in 1 M nitric acid (HNO_3) solution for different times (from 15 min to 20 h). NANOVAK 400 PVD system is used for all metallic film coating and is consist of two sputtering and two thermal evaporator sources. The schematic representation of nanoporous Pt production using the dealloying method is given in Figure 1a. Nanoporous Pt, which dealloyed for 5 h, is heat treated at different temperatures from 200 °C to 500 °C.



(a) (b)

Figure 1. Schematic diagrams of the fabrication of nanoporous Pt with dealloying method (**a**) and resistive gas sensing measurement setup (**b**).

Scanning Electron Microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) that directly attached to the SEM are used to clarify the morphologies of and the composition of nanoporous Pt and Pt-Cu alloy film, respectively. In order to determine hydrogen gas sensing properties, two silver (Ag) electrodes are coated on the top of nanoporus Pt by using a thermal evaporator with a shadow mask for measuring the two-point resistance. Figure 2 shows a schematic illustration for a resistive type sensor device measurment setup. The resistance of nanoporous Pt is continuously recorded by utilizing a two point-probe, with Keithley 2700 multimeter during changing the atmosphere of a home-made measurement cell. The measurement cell is a flow-type aluminum chamber and is included a heatable sample holder. Two mass flow control units (Alicat) are used for controlling hydrogen gas concetration from 10 ppm to 5%. A schematic diagram of hydrogen gas sensor measurement system is given in Figure 1b. Lakeshore 335 temperature controller is used for changing the temperature from 25 °C to 150 °C. All measurement data were recorded using LabVIEW program with a GPIB data acquisition system connected to a personal computer.

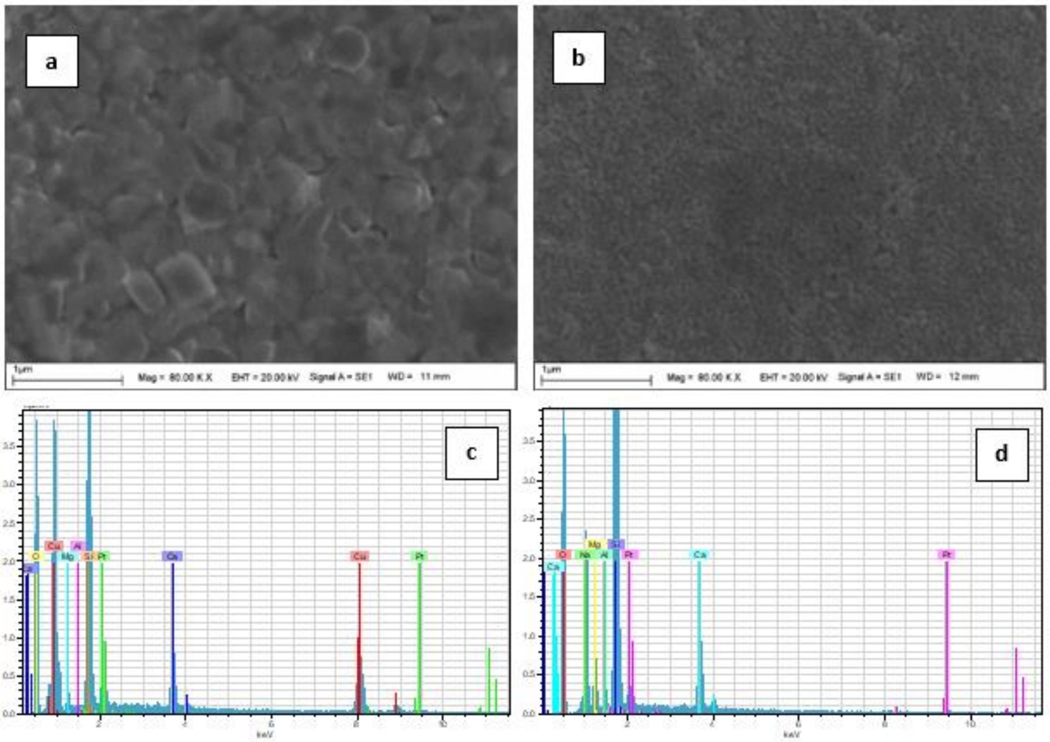


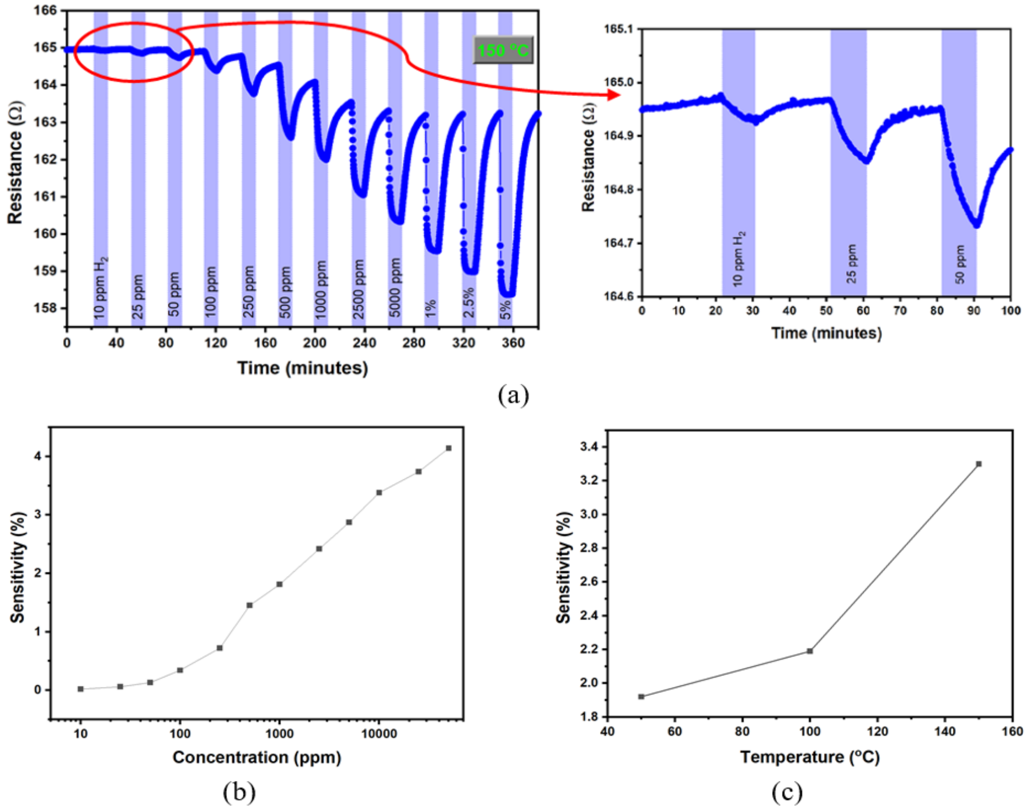
Figure 2. SEM images of Pt-Cu alloy film (**a**) and nanoporous Pt film (**b**) that fabricated with dealloying method in 1 M HNO_3 for 5 h. EDX spectrums of Pt-Cu alloy film (**c**) and nanoporous Pt film (**d**).

3. Results and Discussion

Figure 2a shows SEM image of Pt-Cu alloys before dealloying and Figure 2b shows SEM image of Pt-Cu alloys after dealloying in 1 M HNO_3 for 5 h. According to the sem results, it was seen that the films dealloying for 5 h had a structure of small-grained and smooth porous. EDX spectrum results of Pt-Cu alloy before dealloying and nanoporous Pt etched in 1 M HNO_3 solution for 5 h are given in Figure 2c,d, respectively. The peaks of elements such as Ca, Mg, Al, Si, O, Pt and Cu were determined in the samples prepared according to the EDX results. The peaks of the Ca, Mg, Al and Si elements originate from the material in the structure of the microscope glass substrate. The EDX peaks of Cu and Pt elements come from Pt-Cu alloy film that coated on glass as seen in Figure 2c. When the two graphs are compared, it is understood that when the Pt-Cu alloy containing 85%

Cu is dealloying in 1 M HNO_3 solution for 5 h, Cu is completely removed from the structure. Because there is no peak of Cu element in the EDX results given in Figure 2d. So, It is observed that when dealloyed in nitric acid solution for 5 h, Cu was utterly removed from the alloy and nanoporous Pt with regular pore structure was obtained.

Figure 3a shows the resistance change of nanoporous Pt film during exposure to various hydrogen concentrations in the range of 10 ppm to 5% at the temperature of 150 °C. The resistance of nanoporous Pt film is decreased when the measurement cell is purged with 10ppm hydrogen and then during cleaning of the measurement cell with high purity dry air the resistance increases slowly. Similar behaviors are obtained for the remaining indicated hydrogen concentration. The change in the resistance of nanoporous Pt enhances while hydrogen concentration increases. The hydrogen sensing mechanism could be explained as follow. During the resistance of nanoporous Pt film measurement under dry air flow, the surface of the film is covered with adsorbed oxygen. While hydrogen is exposed to the film, hydrogen atoms dislocate with oxygen atoms, and the number of electron surface scattering decreases. So the decrease in the resistances of the film could be elucidated with the surface scattering phenomenon. Similar behavior was reported for Pt nanowire [17] and Pt thin films [18–20]. Figure 3b shows the sensitivity as a function of logarithmic hydrogen concentration of nanoporous Pt film at 150 °C and the sensitivity is increased as the concentration enhances. Figure 3c shows the sensitivity versus temperature curve of nanoporous Pt exposed to 1% hydrogen. The sensitivity of nanoporous Pt film rises with the temperature, and this behavior could be related to the activation process.



(a)

(b)

(c)

Figure 3. The resistance versus time graph (**a**) and sensitivity as a function of concentration chart (**b**) of nanoporous Pt film exposed to broad hydrogen concentration (10 ppm—5%) at the temperature of 150 °C. (**c**) The sensitivity versus temperature curve of nanoporous Pt exposed to 1% hydrogen.

4. Conclusions

Nanoporous Pt film is successfully fabricated by using dealloying of Pt-Cu alloy thin films that are coated on microscope glass substrates with the magnetron co-sputtering method. Temperature and hydrogen concentration-dependent gas sensing properties of the nanoporous film are studied. Nanoporous Pt film could be potentially used for low concentration hydrogen detection, such as safety issues, hydrogen leak detection, and also detection of molecular hydrogen in exhaled breath for diagnosis.

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References

1. Fasaki, I.; Suchea, M.; Mousdis, G.; Kiriakidis, G.; Kompitsas, M. The effect of Au and Pt nanoclusters on the structural and hydrogen sensing properties of SnO2 thin films. *Thin Solid Films* **2009**, *518*, 1109–1113, https://doi.org/10.1016/j.tsf.2009.07.192.
2. Rane, S.; Arbuj, S.; Rane, S.; Gosavi, S. Hydrogen sensing characteristics of Pt–SnO2 nano-structured composite thin films. *J. Mater.Sci. Mater. Electron.* **2015**, *26*, 3707–3716.
3. Hübert, T.; Boon-Brett, L.; Black, G.; Banach, U. Hydrogen sensors—A review. *Sens. Actuators B. Chem.* **2011**, *157*, 329–352.
4. Zhang, J.; Yang, H.; Martens, B.; Luo, Z.; Xu, D.; Wang, Y.; Zou, S.; Fang, J. Pt–Cu nanoctahedra: synthesis and comparative study with nanocubes on their electrochemical catalytic performance. *Chem. Sci.* **2012**, *3*, 3302–3306, https://doi.org/10.1039/c2sc20514a.
5. You, H.; Yang, S.; Ding, B.; Yang, H. Synthesis of colloidal metal and metal alloy nanoparticles for electrochemical energy applications. *Chem. Soc. Rev.* **2012**, *42*, 2880–2904, https://doi.org/10.1039/c2cs35319a.
6. Lin, H.-X.; Lei, Z.-C.; Jiang, Z.-Y.; Hou, C.-P.; Liu, D.-Y.; Xu, M.-M.; Tian, Z.-Q.; Xie, Z.-X. Supersaturation-Dependent Surface Structure Evolution: From Ionic, Molecular to Metallic Micro/Nanocrystals. *J. Am. Chem. Soc.* **2013**, *135*, 9311–9314, https://doi.org/10.1021/ja404371k.
7. Yamauchi, Y.; Kuroda, K. Rational Design of Mesoporous Metals and Related Nanomaterials by a Soft-Template Approach. *Chem. Asian J.* **2008**, *3*, 664–676, https://doi.org/10.1002/asia.200700350.
8. Zhang, J.; Li, C.M. Nanoporous metals: fabrication strategies and advanced electrochemical applications in catalysis, sensing and energy systems. *Chem. Soc. Rev.* **2012**, *41*, 7016–7031, https://doi.org/10.1039/c2cs35210a.
9. Liang, J.; Du, X.; Gibson, C.; Du, X.W.; Qiao, S.Z. N-Doped Graphene Natively Grown on Hierarchical Ordered Porous Carbon for Enhanced Oxygen Reduction. *Adv. Mater.* **2013**, *25*, 6226–6231, https://doi.org/10.1002/adma.201302569.
10. Chen, A.; Holt-Hindle P. Platinum-based nanostructured materials: synthesis, properties, and applications. *Chem. Rev.* **2010**, *110*, 3767.
11. Kloke. A.; Stetten, F.V.; Zengerle, R.; Kerzenmacher, S. Vertically oriented reduced graphene oxide supported dealloyed palladium–copper nanoparticles for methanol electrooxidation. *Adv. Mater* **2011**, *23*, 4976.
12. Erlebacher, J.; Aziz, M.J.; Karma, A.; Dimitrov, N.V.; Sieradzki, K. Evolution of nanoporosity in dealloying. *Nature* **2001**, *410*, 450–453, https://doi.org/10.1038/35068529.
13. Kertis, F.; Snyder, J.; Govada, L.; Khurshid, S.; Chayen, N.; Erlebacher, J. Evolution of nanoporosity in dealloying. *J. Manage* **2010**, *62*, 50–56.
14. Kunduraci, M. Dealloying technique in the synthesis of lithium-ion battery anode materials. *J. Solid State Electrochem.* **2016**, *20*, 2105–2111, https://doi.org/10.1007/s10008-016-3226-3.
15. Kilinc, N. Resistive Hydrogen Sensors Based on Nanostructured Metals and Metal Alloys. *Nanosci. Nanotechnol. Lett.* **2013**, *5*, 825–841, https://doi.org/10.1166/nnl.2013.1653.
16. Kilinc, N.; Sanduvac, S.; Erkovan, M. Platinum-Nickel alloy thin films for low concentration hydrogen sensor application. *J. Alloy. Compd.* **2021**, *892*, 162237, https://doi.org/10.1016/j.jallcom.2021.162237.

17. Yang, F.; Donavan, K.C.; Kung, S.-C.; Penner, R.M. The Surface Scattering-Based Detection of Hydrogen in Air Using a Platinum Nanowire. *Nano Lett.* **2012**, *12*, 2924–2930, https://doi.org/10.1021/nl300602m.
18. Kilinc, N. Palladium and platinum thin films for low-concentration resistive hydrogen sensor: a comparative study. *J. Mater. Sci. Mater. Electron.* **2021**, *32*, 5567–5578, https://doi.org/10.1007/s10854-021-05279-w.
19. Patel, S.V.; Gland, J.L.; Schwank, J.W. Film Structure and Conductometric Hydrogen-Gas-Sensing Characteristics of Ultrathin Platinum Films. *Langmuir* **1999**, *15*, 3307–3311, https://doi.org/10.1021/la9809426.
20. Şennik, E.; Ürdem, .; Erkovan, M.; Kılınç, N. Sputtered platinum thin films for resistive hydrogen sensor application. *Mater. Lett.* **2016**, *177*, 104–107, https://doi.org/10.1016/j.matlet.2016.04.134.