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# Absorption of N atom in Pd wire at low temperature and the influence on its physical properties

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## Abstract

High temperature in situ resistivity measurement was carried out to monitor the resistivity change of the Pd wire when annealed in the temperature range of 250–400°C in flowing $N_2$. In the range of 250–350°C, the resistivity change with time can be fitted well by a bulk-diffusion model with infinite-long cylinder geometry, the derived apparent diffusion coefficient versus temperature matches the Arrhenius plot well, and the apparent activation energy for this process was derived to be 1.3 eV. The tensile test showed that the mechanical properties of the Pd wire annealed at 300°C in flowing $N_2$ is better than those in air. The results disagree with the traditionally accepted conclusion: nitrogen is insoluble in the Pd below 1400°C (Hansen (1958) Constitution of Binary Alloys, McGraw-Hill, New York). Besides, the influence of superficial oxidation on the absorption and desorption behaviors of N atoms in Pd wire at different annealing temperatures (up to 400°C) was discussed in terms of the reversibility of resistivity change when the ambient atmosphere was changed between pure $N_2$ and air. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Pd wire; $N_2$ adsorption; Resistivity change

## 1. Introduction

More and more electronic devices are used under harsh circumstances, e.g. working at elevated temperature. This brings many new problems for the electronic materials, such as bonding wires. The Pd wire is proposed as a hopeful candidate due to its excellent stability at high temperature [2].

Corrosion resistance and reaction with environmental atmosphere of Pd wire is one of the main factors that influence the mechanical and electrical properties at elevated temperature. Most work on the interaction between Pd and gases at high temperature were focused on the famous Pd–H system [3]. There were only a few reports about Pd–N and Pd–O systems, and these reports were mainly about bulk materials at high temperature (>1000°C). Because the microstructure of the Pd wire differs greatly from its bulk and film counterparts due to its special fabrication process, and that in the future high temperature electronic devices are expected to work at temperatures higher than 250°C (e.g. SiC devices), it is necessary to make a deep investigation on the interaction between the Pd wire and its ambient gases at around 300°C or higher.

In this study, the changes in electrical and mechanical properties of Pd wire during or after annealing in flowing $N_2$ or air around 300°C have been measured by in situ resistivity measurement and tensile test. The changes in resistivity with time were fitted by a bulk diffusion model. The apparent activation energy of this process was derived from the fitting results.

## 2. Experimental procedure

Palladium wires of high purity with a diameter of 25 μm, fabricated by Heraus (Germany), were chosen. The elongation of the wire is in the range of 8–10%.

### 2.1. Resistivity measurement

A schematic of the configuration of sample for in situ resistivity measurement is shown in Fig. 1. Two Si

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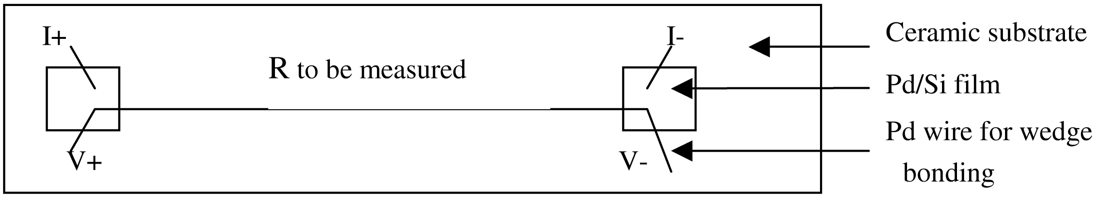

Fig. 1. Schematic diagram of resistivity measurement of Pd wire using the four-point in situ method.

substrates with their top sides deposited with Pd films were adhered to a $Al_2O_3$ ceramic substrate using silver paste. Pd wires were stitch bonded onto the Pd/Si films. Two inner bond points are for voltage measurement, while the two outer bond points are for current connection. Samples were annealed in a quartz tube connected via a switch either to flowing gases (such as $N_2$ and Ar) or air. The online resistance *R* of the wire and temperature *T* were measured by a high-precision Keithley 2001 digital multimeter under the control of a personal computer.

### 2.2. Tensile test

Two groups of Pd wire were annealed at 300°C in air or flowing $N_2$ (purity>99.999%), respectively, for 480 h. The stress–strain tests of the wires were carried out by using a CT-1 fiber-tensile tester (gauge length, 1 cm; strain rate, 1 mm/min).

## 3. Results and discussion

### 3.1. Results of resistivity measurement

The in situ resistivity change of Pd wire with time when annealed at 350°C in flowing $N_2$ and then in air is shown in Fig. 2. The sample was first annealed in air for some time and the resistivity changed slightly. When $N_2$ was switched on, the resistivity of the wire increased immediately, very rapidly at first and became slow finally reaching an almost equilibrium value. When the flowing $N_2$ was shut off and air was let in, the resistivity decreased immediately until it reached its original value. It is demonstrated that the resistivity change is very sensitive to the atmosphere, and the whole process can be repeated. Similar results can also be achieved in the range of 250–350°C.

Obviously, some changes in the microstructure of Pd wire have occurred when annealed in flowing $N_2$ at

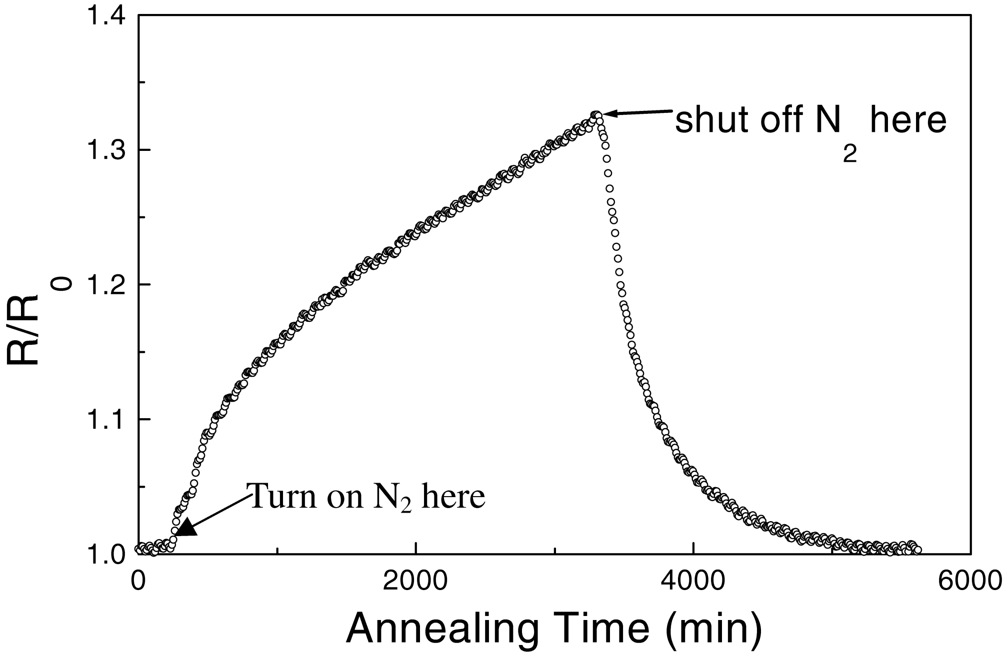

Fig. 2. Relation between resistivity of Pd wire and ambient atmosphere when annealed at 350°C.

elevated temperatures, which in turn caused the change in resistivity, and such a change is almost reversible in the range of 250–350°C. These results disagree with the traditionally accepted point of view drawn from previous studies that nitrogen is insoluble in Pd below 1400°C [1,4]. According to the previous studies, the flowing $N_2$ should have no influence on the resistivity change of Pd wire in this temperature range as we once expected. To explore this phenomenon, we suppose it is the diffusion of N atoms in Pd wire that causes the change in resistivity and this change is proportional to the content of N atoms diffused into the Pd wire (this assumption is reasonable when the content of N atoms in Pd wire is at a low level). In order to interpret fully the change in resistivity, we need to model the diffusion of N through a long cylinder. Suppose also that the diffusion process of N in Pd wire obeys the bulk diffusion model, which neglects the influence of microstructure of the Pd wire, then we can use Fick's second law together with the bulk (cylinder) boundary conditions to fit the resistivity changes.

For infinitely long cylinder geometry, the diffusion flux is limited in the radial direction, so the concentration $c$ is changed only with $r$ and $t$. Fick's second law and the boundary conditions are as follows:

$$\begin{gathered}\frac{\partial c(r,t)}{\partial t} = D\left(\frac{\partial^2 c(r,t)}{\partial r^2} + \frac{1}{r}\frac{\partial c(r,t)}{\partial r}\right) \\ c(r,0) = c_1,\ 0 < r < r_0,\ c(r_0,t) = c_2,\ t > 0\end{gathered} \tag{1}$$

where $c_1$ is the initial concentration of N in the Pd wire, which is a constant; $c_2$ is the concentration of N at the surface of the Pd wire and is also a constant; $D$ is the apparent diffusion coefficient of N in the Pd wire, so the solution of (1) is [5]:

$$\bar{C}(t) = 4c_2\sqrt{\frac{Dt}{\pi r_0^2}} \tag{2}$$

where $\bar{C}(t)$ is the mean concentration of nitrogen atoms in the sample. The total amount of Nitrogen atoms in the sample is $Q(t) = \bar{C}(t)\cdot V$, where $V$ is the sample volume. The resistivity change is supposed to be proportional to the total amount of the nitrogen atoms in the sample, so

$$\begin{aligned}\frac{R(t)-R_0}{R_0} &= K\cdot Q(t) \\ &= K\cdot V\cdot 4c_2\sqrt{\frac{Dt}{\pi r_0^2}} \\ &= K_0 D^{1/2} t^{1/2}\end{aligned} \tag{3}$$

where $K$ is the proportional factor, a constant; and $K_0 = K\cdot V\cdot 4c_2\cdot(\pi r_0^2)^{-1/2}$, also a constant.

Fig. 3 shows the fitting results of the resistivity change with time at 350, 300 and 250°C by using Eq. (3), respectively. It can be seen that the fitting curves fit the experimental results well. The constant in Eq. (3) ($=K_0 D^{1/2}$) can be derived as 0.00455, 0.00193 and 0.00046 $s^{-1/2}$ for aging at 350, 300 and 250°C, respective-

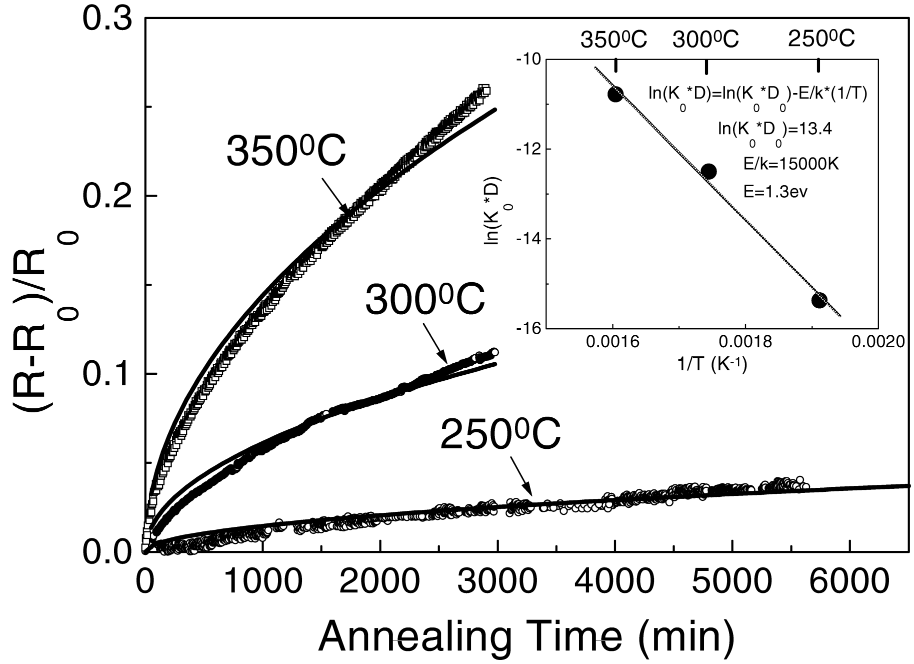

Fig. 3. The relationship between resistivity and time of Pd wire when annealed in flowing $N_2$ at 250–350°C; the solid lines are fitting curves. The embedded figure is the Arrhenius relation fitting curve of the derived apparent $D$ versus temperature.

ly. Besides, as is well known, the relationship between $D$ and temperature $T$ normally follows the Arrhenius relation:

$$D = D_0 \exp(-E/kT) \\ \text{or} \\ \ln D = \ln D_0 + (-E/k)(1/T) \tag{4}$$

where $E$ is the apparent activation energy for the whole process. Fig. 3 also shows the fitting result by using the derived constants of Eq. (4). The Arrhenius activation energy is found to be $E=1.3$ eV (about 30 kcal/mol), which is larger than the activation energy of gases in metals in usual cases [6]. This might indicate that an extra energy corresponding to the dissolution of $N_2$ into N atoms at the surface of Pd bulk body is involved.

As a whole, the resistivity change with time is fitted well with the bulk diffusion theory. However, no direct evidence verifying the existence and the distribution of N atoms in Pd is available either by mass-gain or X-ray-related methods due to the limited sample volume or N concentration in the bulk Pd. So the detailed mechanism of N atoms absorbed in Pd wire is still an open question.

The reversible behavior of the resistivity change during absorption and desorption of N atoms in the range of 250–350°C also indicates that no stable N–Pd intermetallic compound was formed because the resistivity decreased immediately when flowing $N_2$ was shut off. It is further deduced that no Pd-based superficial compound is formed in this temperature range, otherwise it may hinder the reverse behavior of the resistivity change. That the resistivity decreases very rapidly after shutting off the flow of $N_2$ may indicate that the desorption rate of N atoms is much higher than its absorption rate, this is very similar to the case of normal metal–gas systems [6]. An interesting phenomenon which needs further investigation is that when Pd wire is annealed in air, in which the average concentration of $N_2$ is about 80%, the resistivity changes very slightly. This may hint that the activity of $N_2$ molecules in this case is dependent on the purity of the ambient gas.

The influence of even higher annealing temperature on the absorption and desorption behaviors has also been investigated. When Pd wire is annealed at 400°C and the atmosphere is switched between $N_2$ and air, the resistivity versus time curves are different from those at lower temperatures, as shown in Fig. 4. The resistivity changes slightly when annealed in air first, but increases rapidly and soon reaches an equilibrium value when turning on the flowing $N_2$, and it drops almost to the initial value quickly if the flowing $N_2$ is shut off and switched to air. The whole process can be repeated too. But when the temperature is decreased to 300°C and $N_2$ is allowed to flow in again, the resistivity will not change any further. It has been demonstrated [7] that there exists a superficial oxidation when Pd is annealed in air in the range of 350–790°C, so in the present case we can speculate that the superficial oxidation layer hinders the in-diffusion of N atoms, and in turn leaves the resistivity almost unchanged during further post annealing in $N_2$ at 300°C.

### 3.2. Results of tensile testing

Results of tensile testing are shown in Fig. 5. It can be seen that both the elongation and yield stress of the Pd wires decrease after annealing for 480 h in air at 300°C,

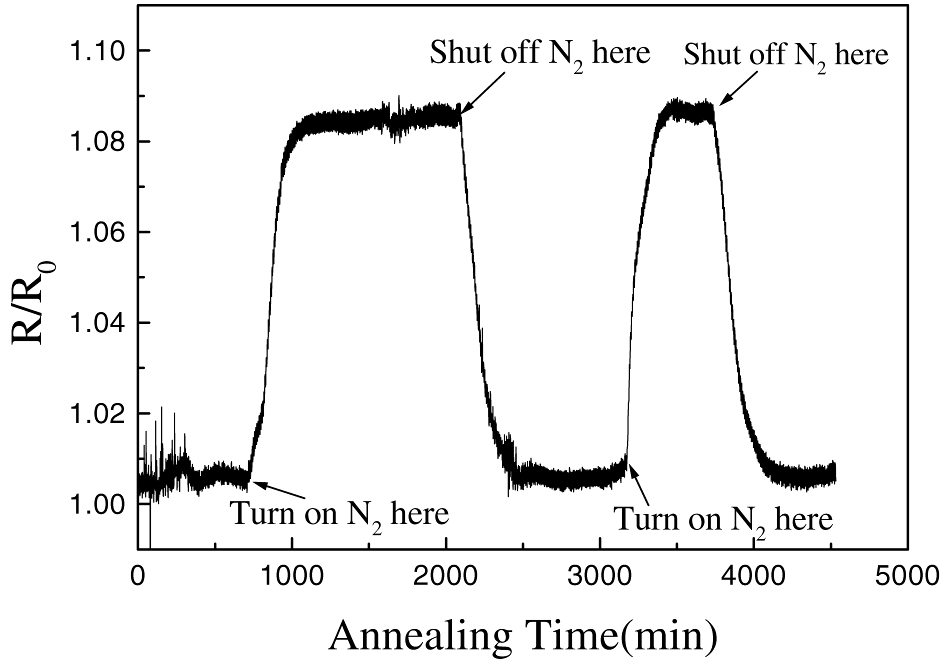

Fig. 4. Relation between resistivity of Pd wire and ambient atmosphere when annealed at 400°C.

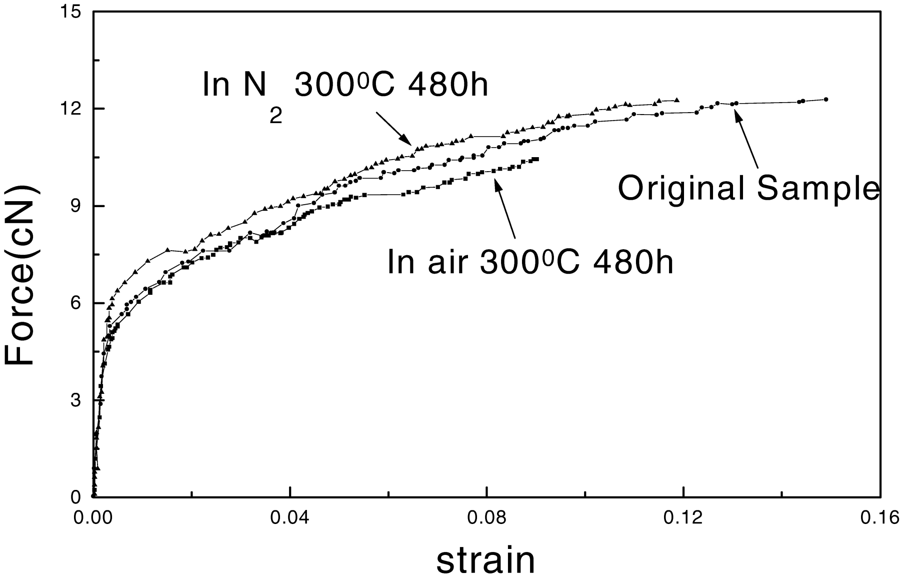

Fig. 5. Tensile–tension curves of Pd wires of as-drawn, annealed for 480 h in air and $N_2$, respectively.

but the yield stress increases after annealed in flowing $N_2$, and the elongation is also better than that of its air counterpart. This demonstrates that the annealing of Pd wire in flowing $N_2$ at 300°C has indeed improved the mechanical properties of the Pd wire, and this may hint that N atoms indeed diffuse into the Pd wire.

## 4. Conclusions

The resistivity of Pd wire changes reversibly when the annealing ambient atmosphere is switched between flowing $N_2$ and air in the temperature range 250–350°C. The resistivity change with time fits the bulk diffusion model with an infinitely long cylinder geometry well. The derived apparent activation energy $E$ for this process, using the Arrhenius relation, is about 1.3 eV. Superficial oxidation is speculated to form if the Pd wire is annealed in air at 400°C. The mechanical properties of the Pd wire annealed at 300°C in flowing $N_2$ is better than its counterpart in air.

## References

[1] P.M. Hansen, in: Constitution of Binary Alloys, McGraw-Hill, New York, 1958, p. 983.
[2] J. Freytag, I. Wennemuth, in: M. Zhang, K.N. Tu (Eds.), Proceedings of 5th International Conference on Solid-state and Integrated Circuit Technology, Publishing House of Electronics Industry, Beijing, 1998, p. 219.
[3] F.A. Lewis, in: The Palladium/Hydrogen System, Academic Press, New York, 1967.
[4] A. Sieverts, W. Krumbhaar, Berlin Deutsch Chem. Gesellshaft 43 (1910) 894.
[5] R. Skomski, J.M.D. Coey, J. Appl. Phys. 73 (11) (1993) 7602.
[6] F. Duan et al., in: 2nd Edition, Metal Physics, Vol. 1, 1987, p. 559, (in Chinese).
[7] K. Othemer, in: Encyclopedia of Chemical Technology, Vol. 15, 1968, pp. 832–860.