Studies of the size of palladium nanoparticles in Pd-C films annealing at different temperatures

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INTRODUCTION

The problem of the hydrogen and also hydrocarbons molecules detection with sufficient sensitivity is very important. The future of aerospace, automobile and energy sectors will revolve around hydrogen fuel. It becomes really important to control and monitor these gases, as there is a huge risk of damage to property and human lives if a leak occurs. Certain gases can be toxic, corrosive or else explosive. So we need sensors that can continuously and effectively detect this gases. In Tele - & Radio Research Institute such films, containing palladium nanograins were synthesized and can be applied as active layer in hydrogen detector.

EXPERIMENTAL

In the PVD process, fullerenes and palladium atoms were deposited on Si under the dynamic pressure of 10^{-5} mbar. Two separated sources were used: one containing fullerene C_{60} powder (99,9 %) and the second with palladium acetate $Pd(C_2H_3O_2)_2$.
During the deposition process the temperature of the substrates was ~ 100 ºC and the time of growth was few minutes. More about this can be found [1,2]. Then some of the PVD samples has been annealed at temperatures 500, 550, 600, 650, 700 and 750ºC. Other samples were modified in CVD process at the same range of temperature. During the second process, a decomposition of the xylene over the film surface occurred. Structure containing Pd nanograins embedded in a amorphous carbon was obtained.

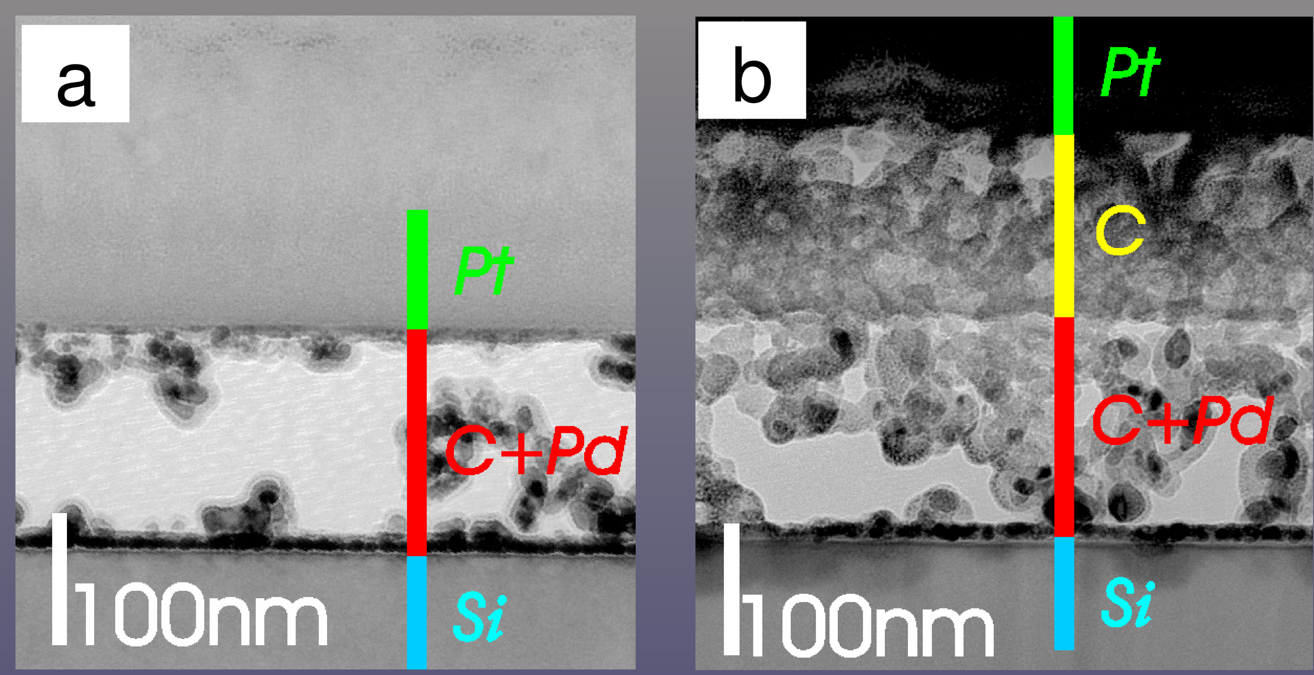

Fig.1. TEM image of the a) PVD and b) PVD/CVD samples.

RESULTS

Fig.1 shows FIB cross sections of the films obtained in PVD and PVD/CVD processes. The films consist of C, C+Pd and Si layers with different thickness and morphology. Cross sections of PVD samples annealed in two different temperature (for example 550˚C and 700˚C) are presented in Fig.2. It is seen that Pd grains are bigger fro annealing samples. The same procedure was carried out for PVD/CVD films. Fig.3. shows the investigated PVD/CVD films also for two temperatures. For all samples histograms of particle size was presented.
In Fig.4 a value of the average size for the both type samples in temperature function were showed. A significant difference in average size of palladium for PVD/CVD samples was noticed. This behavior was caused by existence of graphite shell. The shell is formed around the palladium at temperatures above 600ºC as a result of the decomposition of the organic fraction (eg. xylene), which are clearly visible in the separation of the curves on Fig. 4. at a temperature around 600 ºC The graphite shell is presented in Fig.5. For both types of samples relation described exponential function was obtained. Activation energy was calculated from the Arrhenius formula:

$$D = Kt^n exp(-E_a /RT) = A_0 exp(-E_a /RT)$$

The obtained values of activation energy were: E_{aPVD}: 64,6 ± 1,1 kJ /mol and E_{aCVD}: 38,8 ± 0,9 kJ/mol. For pure palladium nanoparticles were measured similar values 36 kJ /mol [3] or 34,8 kJ/mol [4]. Increase in activation energy was observed for palladium, which is poisoning or contains dopant - 35,3 ± 3 kJ /mol (pure Pd) to 55 ± 11 kJ /mol (sulfur saturated palladium) [5]. In our investigation we had grains of palladium in porous and amorphous carbon (samples after the PVD process) and the grains of palladium in the graphite shell, which are also embedded in a porous carbon (sample after CVD process).

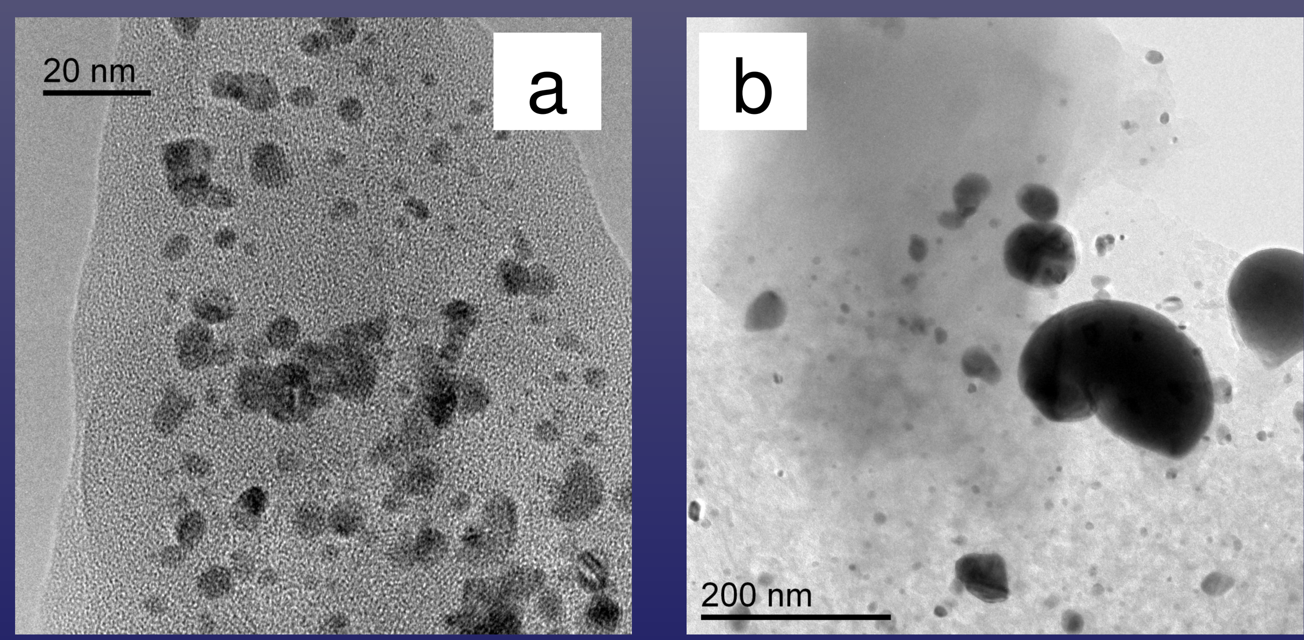

Fig.2. TEM image of the a) PVD sample annealed in 550˚C and b) and 700˚C

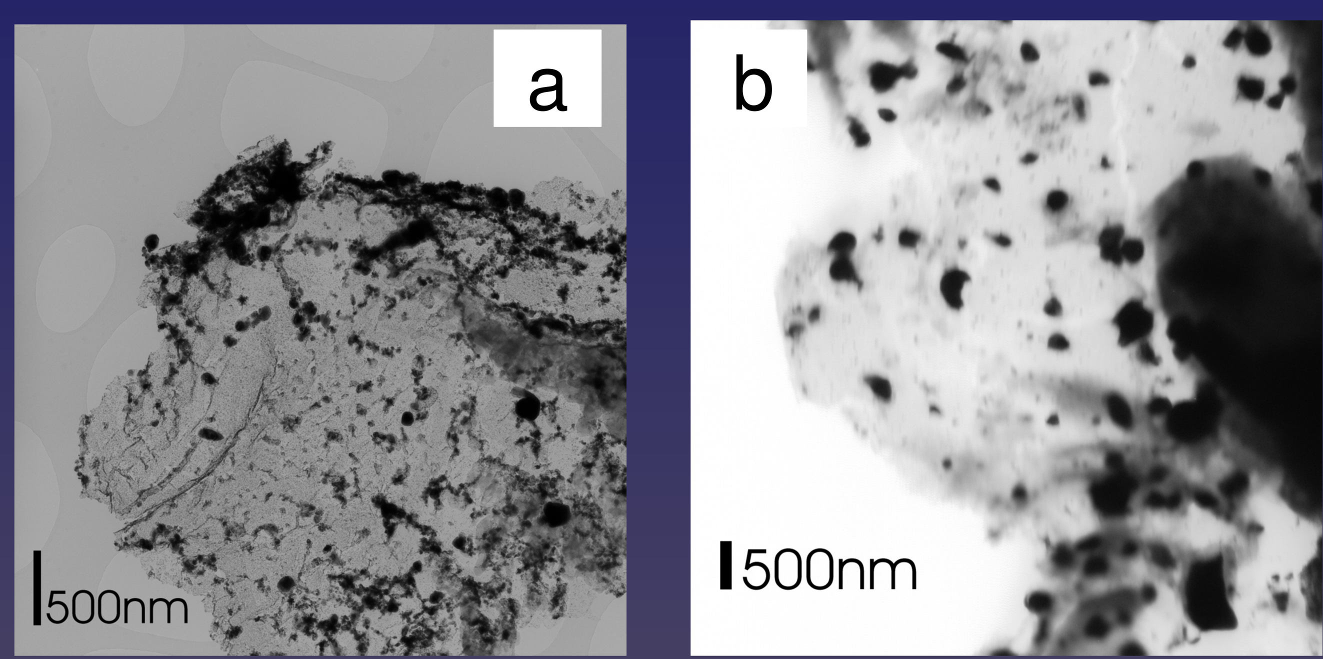

Fig.3. TEM image of the a) PVD/CVD sample annealed in 550˚C and b) and 700˚C

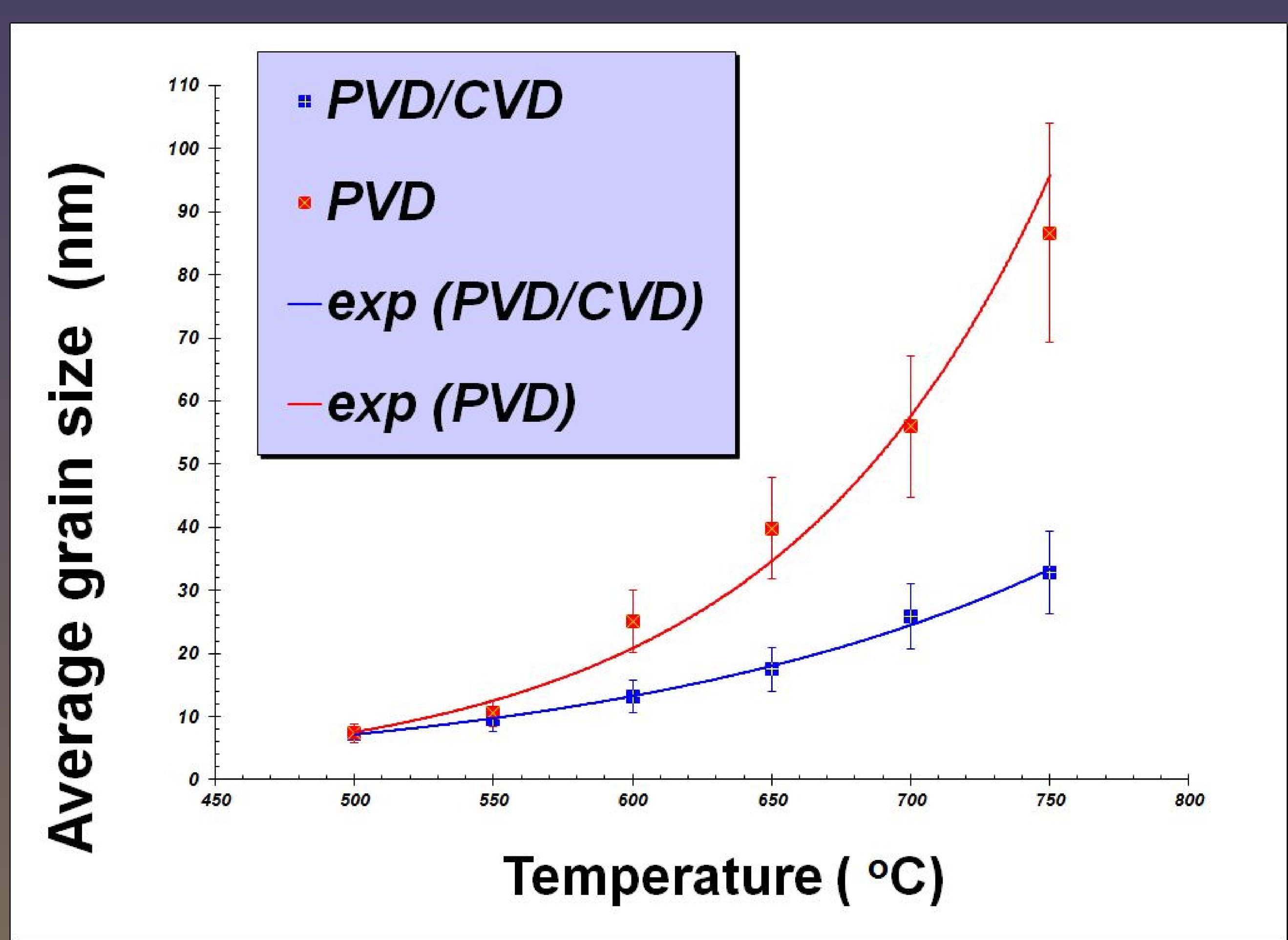

Fig.4. Plot of D vs T for both types of samples of PVD and PVD/CVD

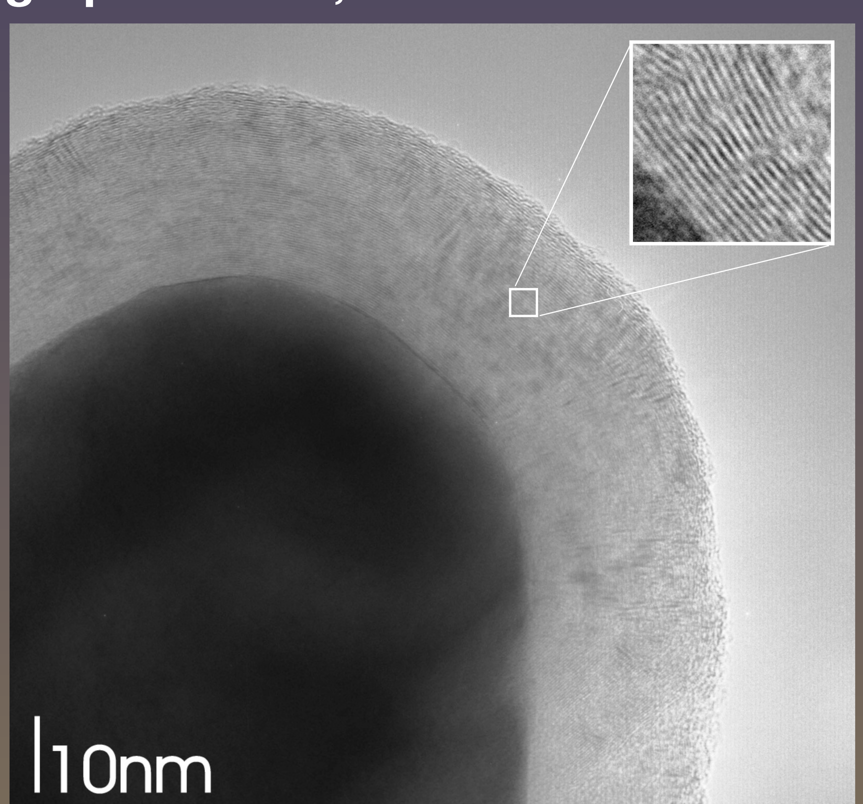

Fig.5. PD particle with graphite shell

CONCLUSIONS

The average particle size was determined as a function of annealed temperature for C-Pd films obtained in two different processes. The difference between the size of palladium in the samples after the PVD and PVD/CVD processes was noted. This diferrence was explained as a existence of a graphite shell. The activation energy from Arrhenius formula was determined. The obtained activation energy values for PVD samples was 64,6 ± 1,1 kJ/mol and - 38,8 ± 0,9 kJ/mol for CVD.

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