ANNEALING TIME EFFECTS ON THE SURFACE MORPHOLOGY OF C-Pd FILMS PREPARED ON SILICON COVERED WITH SiO_2

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Introduction

Morphology changes of C-Pd films prepared in PVD process and next annealed in a temperature of 650oC during different time were studied. These studies were performed with TEM and SEM methods. These films were annealed in the temperature of 923K for 5, 15 and 30 min. Parameters of annealing process are gathered in Tab.1

Sample number	T [K]	t [min]	F_{Ar} [l/h]
F0	-	-	-
F5	923	5	40
F15	923	15	40
F30	923	30	40

Table 1. Annealing processes parameters (T- temperature of annealing , t – process duration time, F_{Ar} – argon flow rate)

C-Pd film after PVD process

It was found that not annealed films are flat and they are composed of grains of with composite character and size 100-200 nm. Pd nanocrystallite of diameter of few nm in some carbon matrix were placed in these grains.

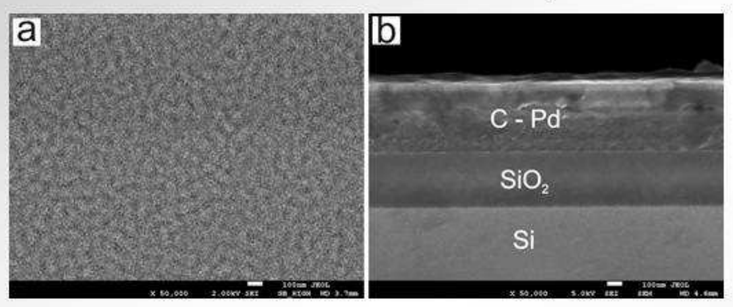


Fig.1. Secondary electron images (SEI) of the surface of F0 film (a) and its cross-section (b)

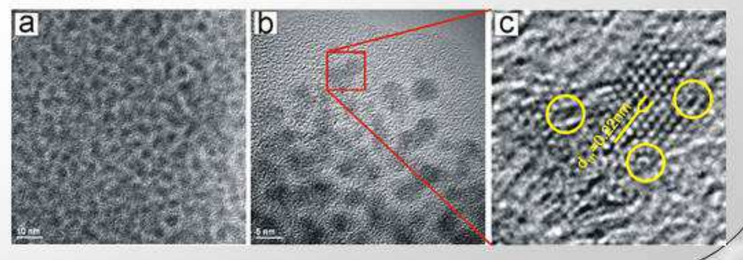


Fig. 2. a, b) TEM images of F0 composite film prepared in PVD process in different magnification c) Pd nanoparticle with marked Pd{111} interplanar spacing

C-Pd film annealed for 15 minutes

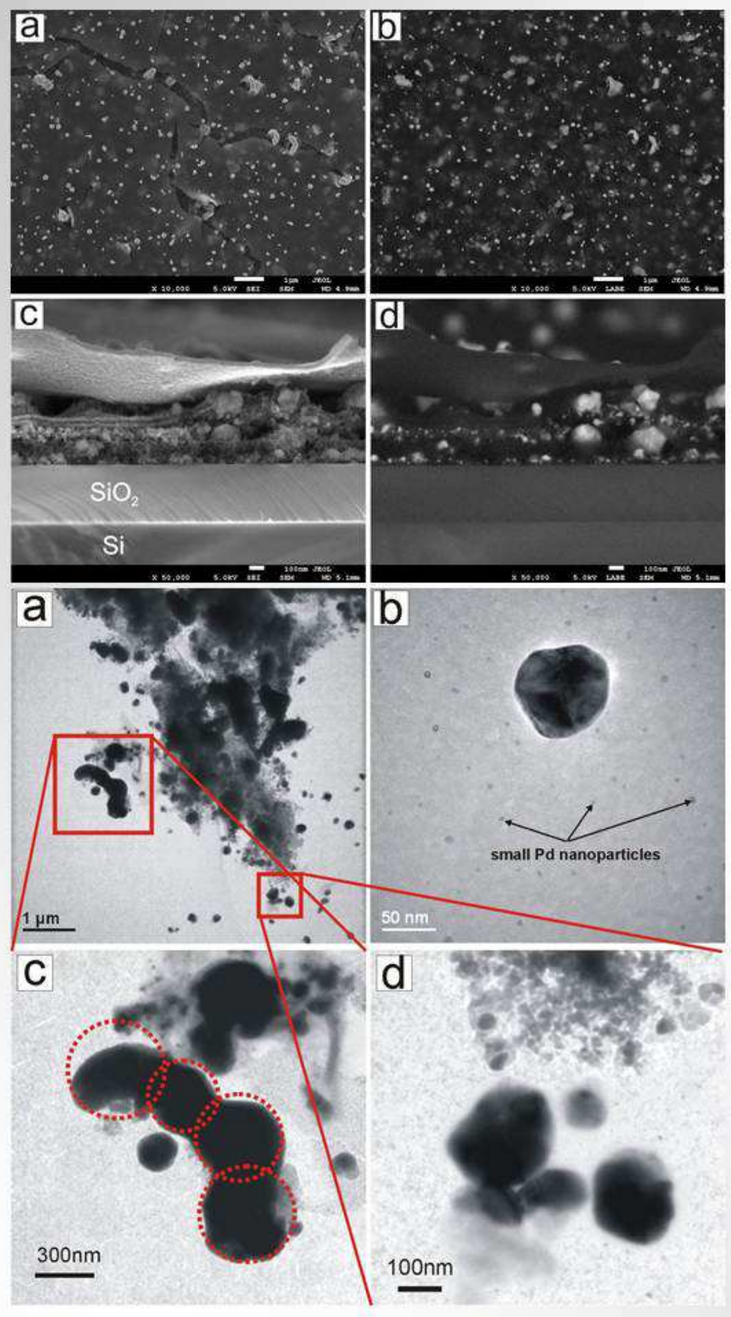


Fig.5. SEM images of F15 film a) SEI of surface, b) LABE image of surface, c) SEI of cross section of film, d) LABE image of cross section of film

Fig.6. a) TEM images for F15 sample b) Pd nanoparticles with different diameter, c) Pd nanoparticles (circles indicated) forming huge Pd grains due to agglomeration process, d) Pd nanoparticles in earlier stage of agglomeration

In samples annealed for 15 min. we found in SEM images Pd nanoparticles with different sizes but most of them is much smaller than in sample F5, although near surface of film some big grain with a length more than 1 mm are also seen (Fig. 5a-d). TEM studies show that the agglomeration process has not been yet ended. These TEM images show big Pd nanoparticles with a diameter of tens of nanometers (Fig. 6a) and small with diameter of several nanometers (Fig. 6b).

C-Pd film annealed for 5 minutes

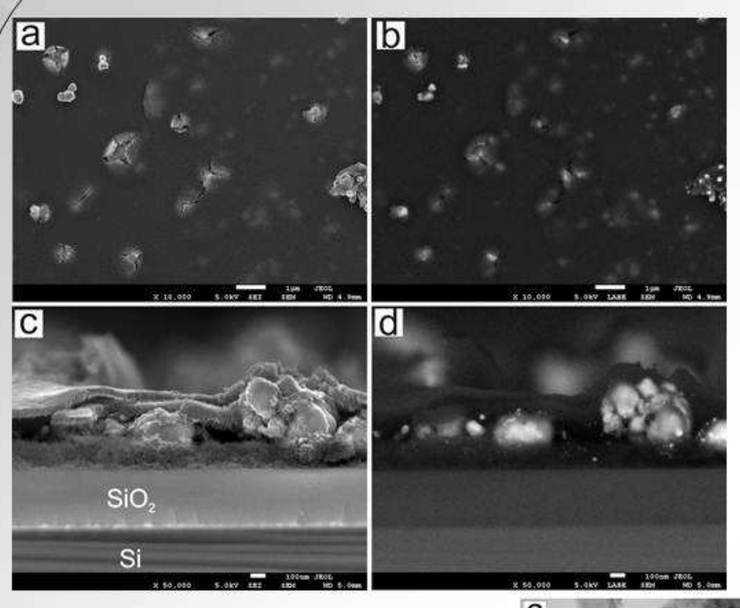


Fig.3. SEM images of F5 film a) SEI of surface, b) LABE image of surface, c) SEI of cross section of film, d) LABE image of cross section of film

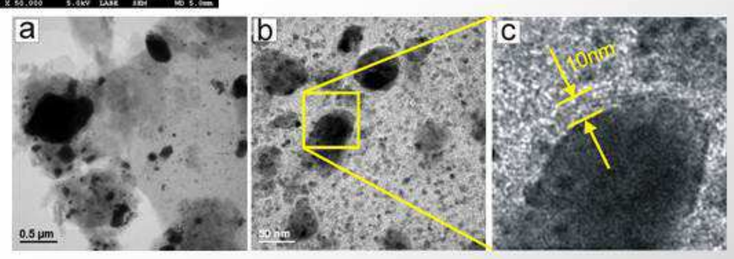
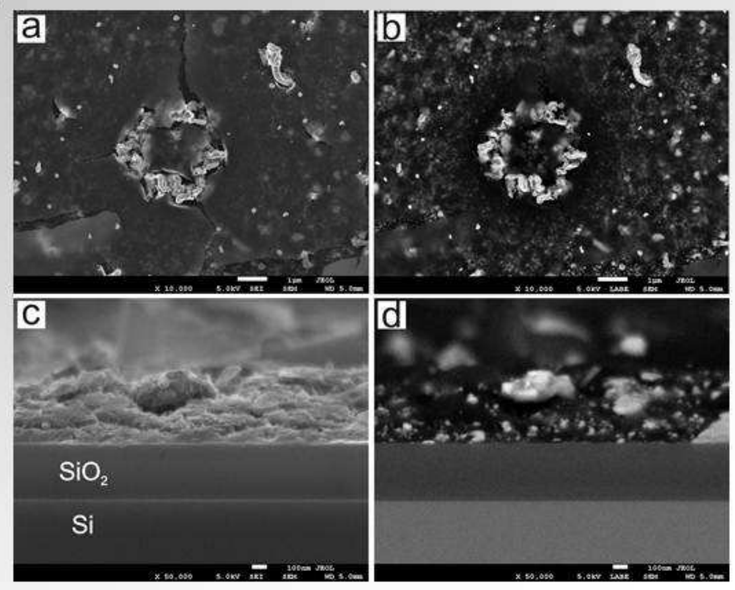


Fig.4. a, b) TEM images of Pd nanoparticles with different diameter, c) graphite shells surrounding Pd nanoparticle

After annealing process lasting 5 minutes small palladium nanoparticles agglomerate into larger ones as well as these big nanograins form a clusters of many grains with sizes up to few hundred nm. Analysis of SEM cross-sectional images made under LABE mode has shown that Pd nanoparticles agglomeration process in a short time of annealing (5 minutes) ran in the middle part of the film.
TEM investigations of F5 sample showed a large disparity in the size of palladium nanoparticles. The largest of them exceeded 200 nm (Fig. 4a), while the smallest had an initial diameter of a few nanometers (Fig. 4b). 5 minutes annealing time was too short to allow for agglomeration of all Pd nanograins. Many of Pd nanoparticles is surrounded by graphite shells that are seen in Fig. 4c. Average thickness is about 10 nm, what means that Pd nanograins is surrounded by odd shells.

C-Pd film annealed after 30 minutes



Film annealed for 30 minutes still has a thin surface carbonaceous layer (Fig. 7a) which is much thinner than this one observe for sample F15 (less than 30 nm). No small nanograins with few nm sizes Pd are anymore seen and carbonaceous matrix becomes more uniform and not divided into sub-layers (Fig. 7d).
TEM observations of F30 samples show many Pd nanograins with a diameter from few tens of nanometers up to few hundred of nanometers, but no one with few nanometers in size (Fig. 8a). The final step of agglomeration process of Pd nanoparticles was observed. The result of this process is shown in the Fig.8b and was marked by circless. No carbon shells were found for this sample.

Fig.7. SEM images of F30 film a) SEI of surface, b) LABE image of surface, c) SEI of cross section of film, d) LABE image of cross section of film

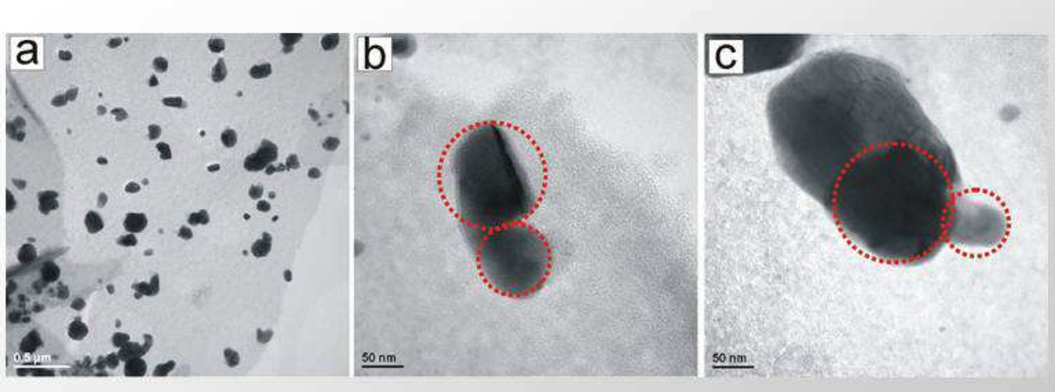


Fig.8. a, b) TEM images of Pd nanoparticles with different diameter b, c) formed agglomerates are presented (circles indicated)

Conclusion

Concluding, we can state that film structure changes with annealing time and increase of this time causes rise of diameter of Pd nanograins what could be connected to agglomeration of Pd nanoparticles process. Due to annealing process, initially flat surface of the C-nPd film becomes rough and decorated with palladium nanoparticles or nanograins that size increases with growing annealing time.
Agglomeration and migration of Pd nanoparticles results cracks and division of film into sub-layers in which Pd nanograins with different sizes are situated.
It was also observed that carbon atoms could be incorporated into Pd lattice (especially on the edge of grains) forming a kind of Pd-C alloys.

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