

Plasma synthesis of catalytic thin films*

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Abstract: Plasma sputter deposition is introduced in the field of catalyst preparation. It is shown that growth kinetics and morphologies are determined by ion to neutral flux ratio and kinetic energies of sputtered atoms. Catalytic activity of such catalysts compares very well with classical catalysts.

INTRODUCTION

Plasma processing is widely used both for material treatments or synthesis and direct gas-phase molecule conversion [1]. This is mainly due to the high reactivity of such a medium for which energetic transfers occur through various forms: excited atoms or molecules, radicals, ions, electrons, etc. Consequently, plasma processes have led to technological developments in the field of surface property modifications and chemical treatments, and application to catalysis is a growing field [2]. Plasma sputtering processing as an alternate way to chemical techniques of catalyst synthesis should be easy to implement and fulfill requirements for compatibility with new regulation of waste control.

EXPERIMENTAL DETAILS

In this context, we have developed a plasma (see Fig. 1) sputter source dedicated to ultrathin metal deposition for catalysis purposes [3]. Briefly, a high frequency (100 MHz) plasma is initiated in argon gas (pressure: 10^{-1} –10 Pa) with an input power of 5 W. The metal atom source is a helicoidal wire that is negatively biased (V_b : –350 to 0 V) with respect to the plasma potential ($V_p \approx 100$ V) so that the Ar^+ ions are attracted and gain sufficient energy to induce sputtering. The substrate is located several centimeters away on a translating holder that reaches a self-bias slightly lower than the floating potential ($V_f \approx 80$ V).

Pd, Pt, Rh, and Pt_xRh_y thin films were deposited on various substrates, amorphous carbon membrane (for transmission electron microscopy observations), SiO_2 native oxide of Si(100) wafers, $\mu\text{-SiC}$, Si_3N_4 thick layers on Si(100). Rh was also deposited on cordierite monolith for testing in methane partial oxidation reaction: $\text{CH}_4 + \frac{1}{2} \text{O}_2 \geq 2\text{H}_2 + \text{CO}$. It was possible to coat inside monolith channels because metal atoms are sputtered with relatively large energy: 2 eV for the maximum of the energy distribution function. This allows the sputtered atoms to diffuse along the inner channel surface.

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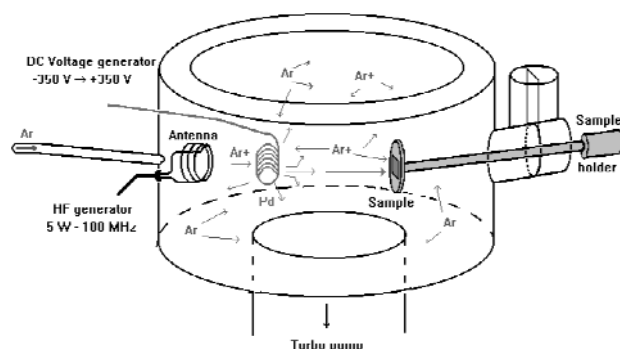


Fig. 1 Sputter plasma deposition experimental setup.

RESULTS AND DISCUSSION

The plasma deposition parameters were observed to be rather different than in chemical processing. The metal atom flux (measured by Rutherford Backscattering) is depending on the sputter ion energy, and the kinetic energy of the depositing atoms is a function of the buffer gas pressure (sputtered neutral atoms leave the target with high kinetic energies; the pressure of the buffer gas controls the number of collision along the target travel path to the substrate and then the kinetic energy). Moreover, the substrate is submitted to an ion flux (measured by Langmuir probe) during the catalytic phase deposition. A complete description of the plasma properties can be found in refs. [4,5]. Chemical analysis using X-ray Photoelectron Spectroscopy and Rutherford Backscattering Spectroscopy indicate that metallic contaminants are present in addition to the deposited active phase. Small quantities of Fe, Cu, Zn (several %) and of Cr, Ni (1 %) have been evidenced as well as carbon and oxygen. The metals originates from residual sputtering of devices present in the chamber such as the antenna, the walls, the wire holder, etc. Their presence does not seem to perturb drastically the growth properties and catalytic activity, because they are not catalysis poisons and, even, may exhibit an activity. Also, the carbon contamination can be removed by a conventional oxidation (O_2)/reduction (H_2) of the catalyst before reaction.

Thin films of transition metals like Pd, Pt, and Rh and corresponding alloys are known to grow via clusters, mainly because cohesive energy is often larger than interaction energy with the support [6]. After completing the maximum possible cluster density, clusters start to coalesce and form meandering structures, which reach percolation.

A very striking feature of our results is that the morphology of the deposited films can be tuned from homogeneously distributed clusters to a continuous layer for low metal contents. Figure 2 displays TEM micrographs describing such behavior for Pd deposition [7].

While plasma conditions leading to Figs. 2a–b give a morphology of isolated clusters with different sizes, Fig. 2c displays a morphology where percolation is already reached. We observed in this case that a continuous layer was formed for a Pd quantity less than $6 \cdot 10^{16}$ at·cm⁻², i.e., a film thickness less than 80 Å (Fig. 2d). Such a continuous film, if reproducible on a suitable support, could be convenient for fabricating membranes required for purifying H_2 before it enters the fuel cell. When varying the deposited quantity (i.e., the deposition time for conditions described in Fig. 2a) the clusters grow and after coalescence a percolating network is reached [7]. The differences displayed by Fig. 2 have been correlated to the ion flux impinging the substrate during the deposition, the deposited atom flux, and kinetic energy. It was then evidenced that ions drive the morphology by direct impact on clusters, which results in controlling the cluster shape. For example, in Fig. 2b, the ion number per Pd atom is greater than in Fig. 2a, resulting in a greater cluster size for a same deposited quantity. Large kinetic

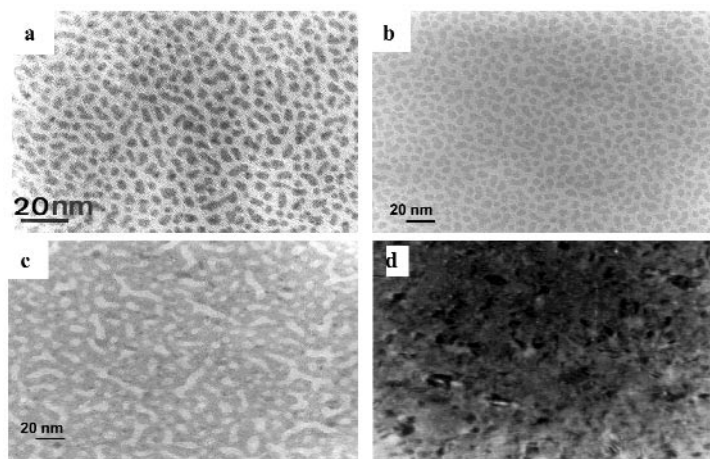


Fig. 2 TEM micrographs showing Pd deposits for four plasma conditions leading to a quantity of 10^{16} at·cm⁻². Dark zones are Pd-covered areas. (a) $E_{Pd} = 0.026$ eV, $\phi_{Ar}^+/\phi_{Pd} = 3$, $\langle d \rangle = 3.5$ nm; (b) $E_{Pd} = 0.026$ eV, $\phi_{Ar}^+/\phi_{Pd} = 17$, $\langle d \rangle = 4.4$ nm; (c) $E_{Pd} = 1.2$ eV, $\phi_{Ar}^+/\phi_{Pd} = 8$, $\langle d \rangle$ is not defined due to percolation; (d) same as (c), but for a slightly larger deposited quantity: $6 \cdot 10^{16}$ at·cm⁻² (i.e., 8 nm). In that case, the film is already continuous. ($\langle d \rangle$ is the mean cluster diameter).

energy of depositing atom was deduced to be responsible for obtaining the continuous Pd film at very low content due to increasing mobility allowing efficient finding of anchoring sites [7,8]. Similar evolutions have been also obtained for Pt, Rh, and Pt_xRh_y deposits.

CATALYTIC ACTIVITY

Catalytic activity of such deposits was examined for two reactions: the low-temperature (25 °C) 1,3 butadiene hydrogenation with Pd catalysts [9] and high-temperature (900–1200 °C) partial oxidation of methane for syngas production. In the first case, it was demonstrated that plasma sputter deposited catalysts were as active as those obtained by conventional chemical techniques [9]. In the second case, the selectivity toward hydrogen was around 25 % for Rh catalysts supported on cordierite monolith without washcoat at reaction temperature $T = 1200$ °C. Conversion of methane was 35 % and oxygen 90 %. Selectivity toward other products was: CO 100 %, CO₂ 0 % and H₂O 75 % (percentages are defined as CO + CO₂ = 100 % and H₂ + H₂O = 100 %). When comparing to chemical techniques, the conversion of methane and selectivity toward H₂ are less efficient. The low contents of the catalysts ($8 \cdot 10^{15}$ at·cm⁻²) is expected to be responsible for such low performances. But the high selectivity toward CO suggests that the direct mechanism (no reforming step) is important. On the other hand, a positive point is that these catalysts are very stable at this temperature and among reaction time. The loss of metal content, as measured by RBS after reaction, is only 25% while for chemical technique, it is 75 %. Moreover, there is no inward diffusion of metal. If we remember that there is no washcoat, it means that the plasma creates some special sites, which allow the stability of the deposits.

CONCLUSION

Summarily, we have developed a plasma sputter deposition source dedicated to catalytic thin film growth. Ion flux on the sputtering wire, responsible for metal atom sputtering can be tuned without modifying the ion flux impinging the substrate during growth. At the same time, kinetic energy of the

sputtered atoms can be varied in a large range (0.026 eV to a few eV depending on the plasma pressure and on the sputtered metal).

This allows different deposition conditions contrary to chemical impregnation and classical vacuum evaporation for which these parameters remain fixed. The same deposition rate can be obtained with different plasma deposition conditions allowing a great versatility regarding to morphology of the obtained films. The possibility for tuning the growth from clusters to very low thickness continuous film of palladium has been demonstrated. On the other hand, the evolution of cluster radius against deposition time has shown that both ion flux and sputtered atom kinetic energy drive the growth in a coupled way. The relevant parameters have been identified to be the ratio of ion flux to the deposition rate and the sputtered atom kinetic energy. Finally, good catalytic properties have been obtained both at low and high reaction temperature.

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