

Fabrication of Porous Platinum Thin Films for Hydrocarbon Sensor Applications

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We have demonstrated the fabrication of porous Pt films prepared by a new technique known as glancing angle deposition (GLAD). This method can be used to produce engineered thin films with high surface area, having microstructures typically characterized by high-aspect-ratio, nanometer-scale pillars. The catalytic efficiencies of selected samples were evaluated, and it was found that the GLAD-based Pt films exhibited catalytic properties superior to those of sputtered Pt films.

1. Introduction

Recently, a considerable amount of time has been spent investigating new methods of producing porous thin films of a variety of materials.⁽¹⁻³⁾ One such material that could benefit greatly from new deposition methods is platinum. Pt films have been used as electrodes or catalysts in a wide variety of applications, such as sensors,^(4,5) direct methanol fuel cells,^(6,7) and electrochemical deposition systems.⁽⁸⁾ The enhanced porosity (and surface area) resulting from new deposition methods has the potential to make significant improvements to the Pt films used in these applications.

Hydrocarbon sensing technology is one notable area where high surface area films are essential. To rapidly detect hydrocarbons at low concentrations, as found, for example, in automotive emissions, technologies such as silicon-based microcalorimeters have been developed.⁽⁹⁾ These devices are simply resistance elements for temperature measurement

patterned on two thin Si membranes. One membrane is covered with a catalyst material, while the other is left bare to establish a reference temperature. The oxidation of hydrocarbons at the surface of the catalyst-coated membrane elevates the temperature with respect to that of the reference membrane, thus providing a measure of the concentration of the hydrocarbons present. To achieve good sensitivity from this type of sensor, it is crucial to incorporate a catalyst having high activity and large surface area. In addition, these materials must be suitable for integration onto small, micromachined silicon devices. Obviously, these constraints pose challenges for catalyst development. Conventional catalyst materials, such as noble metals dispersed over high surface area alumina,⁽¹⁰⁾ are not easy to integrate with standard microfabrication techniques and, furthermore, do not adhere well to the Si-based structures. On the other hand, catalyst coatings, such as sputtered noble metal films, which adhere well and are easy to prepare, tend to have surface areas that are orders of magnitude too small for adequate sensor sensitivity.

In this paper, the preparation of high porosity films by a new technique known as glancing angle deposition (GLAD) is discussed, and, in addition, an initial investigation of the catalytic properties of such films is presented.

2. Materials and Methods

During the earliest phases of film growth, it is known that the formation of continuous film layers is preceded by the clustering of atoms into small nuclei.⁽¹¹⁾ With conventional evaporation techniques, as additional atoms strike the surface, these nuclei grow outwards until they meet one another, thereby forming a complete layer. This, however, does not occur during GLAD. In this case, substrates are placed at a highly oblique angle ($>80^\circ$) with respect to the direction of incident flux. Under these circumstances, any random, vertical variations in the film become enhanced, i.e., the areas behind the nuclei lie in the "shadows" of the nuclei and are thus prevented from receiving additional flux.⁽¹²⁾ As a result, growth of the film occurs preferentially above rather than around the initial nuclei. Once the deposition is complete, the result is a microstructure consisting of high aspect ratio posts, inclined in a direction toward the vapor source.

The directionality of the inclined columns is often exploited in the production of additional, unique microstructures. A helically microstructured thin film,⁽¹³⁾ for instance, may be produced by slowly rotating the substrate about the axis perpendicular to its center, while simultaneously holding the incident flux at a constant, highly oblique angle. Under these conditions, the position of the "near side" of the growing columns constantly changes, forcing the direction of growth to change correspondingly. Additional details describing the GLAD technique and the microstructures which may be produced can be found in the literature.⁽¹²⁻¹⁷⁾

For this experiment, porous Pt thin films were deposited by the GLAD technique using electron beam evaporation onto single-crystal silicon wafers. During the evaporation, the surface normal of the wafers was maintained at a constant angle of 85° with respect to the direction of incident flux, while the wafers were rotated about axes normal to their

surfaces. The Pt film shown in Fig. 1(a) consists of a 1.2 turn (432° of rotation) helical film of pitch 215 nm. The total thickness is 260 nm. The system base pressure during this deposition was approximately 1×10^{-4} Pa.

As in all electron beam evaporations which proceed without substrate cooling, the temperature at the substrate during GLAD tends to increase throughout the deposition. A small thermocouple thermally bonded to a stationary substrate was used to measure the rise in substrate temperature. On average, 1.9 kW of power was delivered to the evaporant during two consecutive depositions. The maximum substrate temperature observed over this period was 149°C .

This heating effect has implications for film growth. As the temperature rises, the average adatom diffusion length increases. Since atoms are able to move greater distances before finding a permanent place in the structure, the self-shadowing mechanism becomes less dominant, and the film porosity decreases. Macroscopically, this reduction manifests itself in films as thickening columns; however, since the melting point of Pt (1769°C) is substantially higher than the maximum substrate temperature, this effect is expected to be minimal.

Intercolumn competition is another factor creating a tendency toward broader columns. Even in the final stages of deposition, random processes remain in effect. Often particular columns accumulate sufficient material to completely engulf neighboring columns in their shadows. Receiving no additional flux, growth of the slightly smaller columns is terminated, while the slightly larger columns begin to expand laterally into the vacated space. The larger column thus becomes thicker. For thick ($>0.5 \mu\text{m}$) films, columnar broadening leads to reduced differential surface area at points greater distances from the substrate. Since the films grown for this experiment are fairly thin, it is difficult to discern any thickening of the helical structure. However, efforts to increase the total surface area of

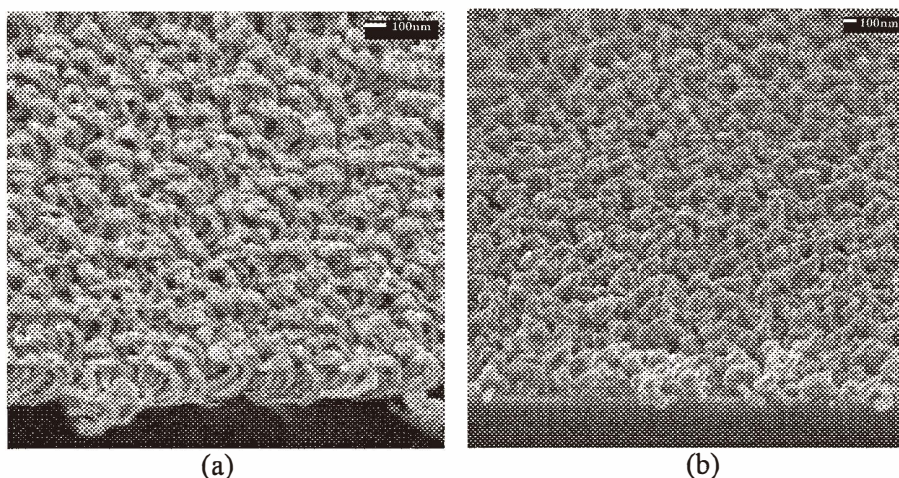


Fig. 1. SEM images of the Pt GLAD film (a) prior to and (b) following annealing at 600°C .

catalytic GLAD Pt films by increasing the film thickness will be slightly impeded by broadening behavior.

After deposition, each sample to be tested was cleaved from the wafer and, in an effort to stabilize the grain and microstructure of the film, annealed in air at a minimum temperature of 600°C for one hour. Scanning electron microscope (SEM) images of the same Pt samples were taken both before and after annealing (Figs. 1(a) and 1(b)). The annealed Pt films showed three notable differences when compared to the as-deposited films. First, smaller Pt columns and nuclei on the substrate of the as-deposited film had agglomerated during the annealing process, leaving the substrate clear of the “undergrowth” that is common in GLAD films. (This “undergrowth” is the result of competition between small columns during the initial stages of film growth, before self-shadowing becomes well established). Second, the helices themselves suffered some agglomeration such that the helical structure was barely evident, or completely destroyed. Finally, the film thickness declined slightly from 260 nm to 230 nm. However, as may be seen in Fig. 1(b), the films did maintain a high geometrical surface area during the anneal.

Representative samples of the Pt GLAD films deposited on Si substrates were evaluated for their catalytic performance in a gas flow reactor. For the microcalorimetric sensor application described above, conversion efficiencies for typical automotive exhaust species (CO, H₂, CH₄, C₃H₆, C₃H₈ and NO_x) are normally measured as a function of a variety of parameters, such as temperature and redox ratio (the ratio of reductant to oxidant concentrations in the gas mixture). In this initial set of experiments, data were acquired with either 0.5% CO, 0.1% C₃H₆, or 0.1% C₃H₈ as the combustible species. Computer-operated mass flow controllers were used to combine the combustible components with oxygen at a redox ratio of 0.5 and N₂ as a carrier gas to bring the total gas flow to 250 sccm. A fine thermocouple located adjacent to the sample measured its temperature. The reaction furnace was ramped at 10°C/min to ~500°C and then allowed to cool slowly back to room temperature. Concentrations of the combustible species were measured downstream of the reactor with gas analyzers from Rosemount Analytical. From the measured gas concentrations, conversion efficiencies were determined.

For gas flow conditions typical of the intended microcalorimeter use, observed conversion efficiencies can depend upon the geometric size and orientation of the sample in the gas flow stream. To address this issue, care was taken to mount every sample in an identical fashion in a reactor made from quartz tubing having a rectangular, rather than circular, cross section, as is illustrated in Fig. 2 below. Identically-sized samples were then compared against a reference sample in a systematic, repeatable fashion. Our reference catalyst consists of a 1 cm² longitudinal slice removed from a commercially available automotive honeycomb monolith. This sample is a ceramic supported Pd-based catalyst, which was chosen due to its known high activity, surface area and noble metal dispersion.^(a)

In this experimental configuration, an equation describing the approximate behavior of a sample's conversion efficiency may be derived by combining fundamental equations for the rate of reactant consumption, the Arrhenius rate constant, the gas residence time, the diffusion equation, and the temperature dependence of the diffusion coefficient.⁽¹⁸⁻²⁰⁾ The result is:

^(a)Supported refers to catalysts where small clusters of catalytic atoms are dispersed on the surface of another material. The support tends to have high surface area, leading to a large catalyst surface area. In many cases, chemical interactions between the support and catalyst are involved in the catalytic reaction. Non-supported, in contrast, refers to catalytic materials having a physical structure, not including the substrate, formed entirely of the catalyst itself. These materials are most often mechanically continuous and are not reliant upon the substrate during reactions.

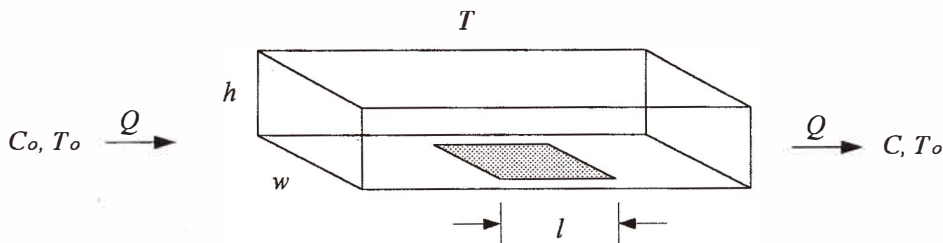


Fig. 2. Schematic drawing illustrating the placement of the catalyst sample within the gas flow reactor.

$$\eta = \sqrt{\frac{2D_0lw}{hQ} \left(\frac{T}{T_0}\right)^{0.75} \left[1 - \exp\left(-\frac{k_0T_0lwh}{Q} \frac{e^{-E/kT}}{T}\right)\right]}, \quad (1)$$

where l , w and h are the dimensions of the reactor, D_0 is the coefficient of binary molecular diffusion, Q is the volumetric flow rate of the gas, T is the gas temperature in the reactor, T_0 is the gas temperature at the location of the mass flow controllers, k_0 is the rate constant for the reaction, k is the Boltzmann constant, and E is the activation energy for the reaction.

At low temperatures, reactions are kinetically limited and the conversion efficiency increases roughly exponentially with temperature. At higher temperatures, however, the reaction becomes mass transport (reactant to catalyst) limited, and the conversion efficiency increases only modestly with temperature. For our purposes, the most relevant parameter is the "light-off temperature," defined as the temperature at which the conversion efficiency reaches half of the mass transport limited value. The light-off temperature is related to the catalyst activity and the number of catalytic sites available on the sample, with a low light-off temperature being indicative of a good catalyst.

3. Results and Discussion

By measuring the mass of a small ($\sim 145 \text{ mm}^2$) Si substrate both prior to and following film removal, we were able to estimate the density of the Pt coatings. The substrate, after mechanical polishing and chemical etching, decreased in mass by $192 \mu\text{g}$. From SEM images, the film thickness was known to be 260 nm , which leads to a density estimate of 5.11 g/cm^3 . This value is 23.8% of the known bulk density of Pt and is indicative of significantly increased porosity in the GLAD films. This density value is consistent with values obtained for GLAD films fabricated of other materials.⁽¹⁴⁾

Attempts to measure the surface area of the specific films tested for catalytic activity were unsuccessful; however, similar films composed of different materials were found to have surface areas ranging from 24 (for $110\text{-nm-thick TiO}_2$ films) to 517 (for $4.5\text{-}\mu\text{m-thick}$

SiO₂ films) times the geometrical area of the sample.⁽²¹⁾ It is likely that the GLAD films described in this paper have surface areas in the lower end of the range.

Light-off curves for a Pt GLAD sample are shown in Fig. 3. The data sets for each combustible species were collected independently, beginning with CO and followed subsequently by C₃H₆ and C₃H₈. These species were chosen for the initial tests since they most closely represent the primary constituents found in automotive exhaust. Among them, CO is the easiest to catalyze, C₃H₆ is representative of the "fast-burning" family of unsaturated hydrocarbons, and C₃H₈ is representative of the "slow-burning" family of saturated hydrocarbons. Data were acquired with excess oxygen ($R=0.5$) in the gas stream. This was done to avoid peculiarities that might arise near stoichiometry, either from the limited accuracy of the mass flow controllers or from the underlying kinetics of the reaction.

The Pt GLAD catalyst shown in Fig. 3 lights off in CO at ~340°C, and for temperatures between 360°C and 420°C, oscillations are observed in the CO conversion efficiency. The catalyst lights off in C₃H₆ at ~360°, a slightly higher temperature than for CO. For C₃H₈, the catalyst initially lights off at ~270°C. In contrast to CO and C₃H₆, however, hysteresis is observed in the C₃H₈ conversion rate as the sample is cooled. Furthermore, each subsequent run (not shown in graph) yields a reduced efficiency, until ultimately no conversion whatsoever is observed.

In an attempt to identify the mechanism responsible for the reduction of efficiency, SEM analysis was once again employed. However, no remarkable observations could be made. Surface carbon deposits were not visible in the images, and no evidence of

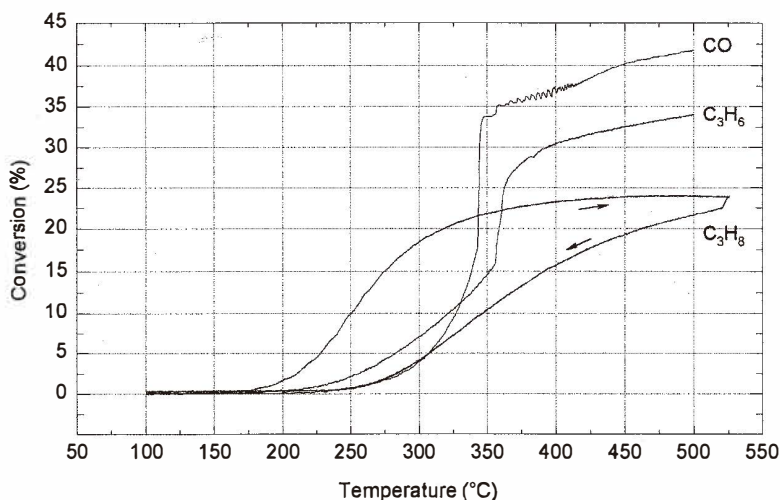


Fig. 3. Conversion efficiency as a function of temperature for the Pt GLAD sample. Data were obtained at $R = 0.5$ with 0.5% of CO or 1,000 ppm of C₃H₆ or C₃H₈ in a N₂ carrier gas at a flow rate of 250 sccm.

additional column agglomeration could be found. We are unable at this time to suggest any explanation for the degradation in catalyst performance following a C_3H_8 conversion experiment.

Because conditions of enhanced shadowing will be in effect so long as substrates are held at highly oblique angles, thicker Pt films deposited by the GLAD technique will have greater surface areas.⁽²¹⁾ Thus, through the addition of catalytic sites, an increased film thickness leads to an increased rate constant κ_0 , which in turn may lead to improved conversion efficiencies and reduced light-off temperatures. If, however, conversion is limited by the diffusion of reactants through the porous structure to the catalytic sites, increasing the number of sites will not necessarily improve the conversion.

Other non-supported Pt film samples exhibit behavior similar to that observed for the Pt GLAD film. The results from a 50-nm-thick Pt film deposited on Si by sputtering at normal incidence are shown in Fig. 4. Because this film was deposited at normal incidence, atomic shadowing was not a dominant film growth factor, and the film lacks the enhanced surface area of the GLAD sample. The light-off profiles display the same general form as those seen from the GLAD sample. Characteristics such as the appearance of high-temperature oscillations in the CO conversion rate, the hysteresis in C_3H_8 conversion, and the reduction (not shown) and eventual cessation of C_3H_8 conversion are all present in the data gathered from the sputtered sample. This sample was, however, slightly less active, having average light-off temperatures $\sim 25^\circ C$ higher than those of the GLAD sample.

Several previously tested, supported Pt catalysts have exhibited better catalytic performance than either the GLAD or sputtered Pt samples discussed above.⁽²²⁻²⁶⁾ Results, for

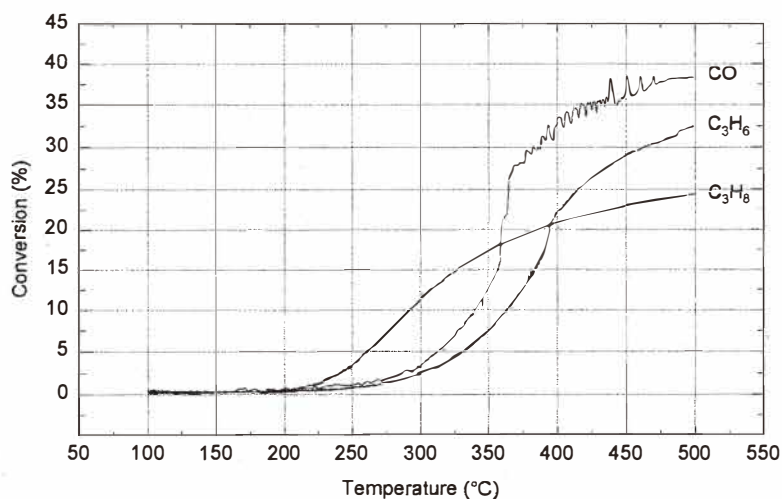


Fig. 4. Conversion efficiency as a function of temperature for a 50 nm sputtered Pt film on a Si substrate. Experimental conditions were identical to those described in Fig. 3.

example, were also collected from a more conventional catalyst, formed from Pt dispersed on high surface area alumina powder. These data are shown in Fig. 5. For CO and C₃H₆, light-off temperatures were, respectively, 255°C and 265°C. For C₃H₈, the light-off temperature was more difficult to assess, since the conversion efficiency for this species is relatively poor and didn't reach half its mass transfer limit during the test. Unlike the unsupported Pt samples, results from these supported films are reasonably reproducible and do not exhibit significant degradation in performance upon extended exposure to C₃H₈. Other noticeable differences include less abrupt light-off transitions and the lack of oscillations in the high-temperature CO conversion efficiency. However, it must be recalled that these materials are not as compatible with silicon microfabrication integration techniques.

Obviously, many of the differences observed between the unsupported (GLAD and sputtered) and supported Pt catalysts can be attributed to the size and microstructure of the Pt particles in the samples. Metal-support interaction can also be an important part of the catalytic reaction. In addition, the support is often capable of storing oxygen and performing other catalysis-enhancing functions. The supported catalysts are characterized by small, well-dispersed Pt grains, while the unsupported catalysts are characterized by much larger Pt grain sizes and a higher degree of crystallinity. This claim is consistent with the observed CO conversion behavior, since self-sustained CO oscillations on crystalline and polycrystalline Pt surfaces are well known and documented extensively in the literature.⁽²⁷⁾

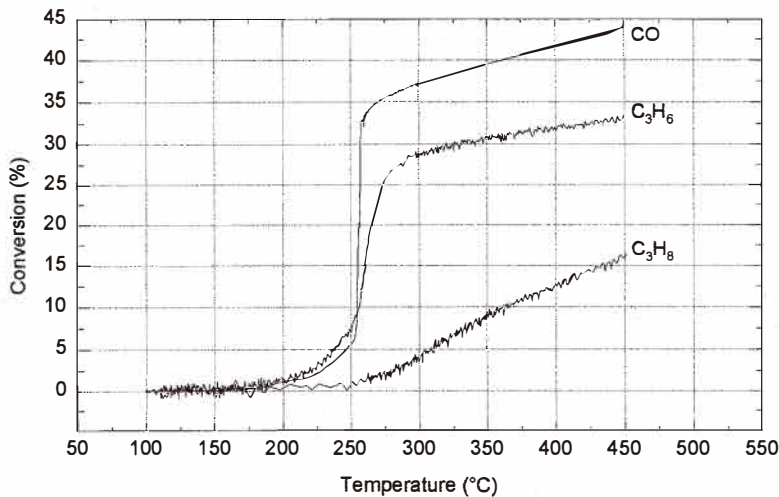


Fig. 5. Conversion efficiency as a function of temperature for a conventional-type alumina supported Pt catalyst. Experimental conditions were the same as those described in Fig. 3.

4. Conclusions

GLAD films of platinum have been shown to effectively catalyze reactions involving three undesirable constituents of automotive exhaust, CO, C₃H₆, and C₃H₈. Porous thin film samples of Pt produced by the GLAD technique exhibited catalytic properties superior to those of sputtered Pt films. On average, light-off temperatures from GLAD films were 25°C lower than those from simple sputtered films, and it is likely that this value could be further improved with thicker films. Results from the GLAD catalysts were not as good as those from previously tested, alumina supported Pt samples; however, the latter catalyst type is less suitable for integration with Si-based microcalorimeter technology.

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