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Effect of Annealing Temperature on the Optical Properties of Palladium Thin Film

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ABSTRACT

In this paper, the effect of annealing temperature on the optical properties of palladium thin films has been investigated. The Pd thin films with thickness of about 123 Å were deposited on glass substrates by electron beam coating method. Then the palladium thin films were annealed in air at 350˚C, 450˚C, 550˚C and 650˚C for 1 h and then cold slowly. All the initial Pd films were found to have amorphous structure. Their optical properties were studied as function of annealing temperature using Ultraviolet-Visible (UV-Vis) spectroscopy. The direct band gaps in Pd films have been determined. Decreasing the values of the direct band gap shows also increasing the Pd crystallite nanostructure with increasing annealing temperature.

Keywords: Pd Properties; Coating; XRD; Band Gap; Annealing; Crystallite Nanostructure

1. Introduction

The structure and microstructure of systems containing nanoparticles have recently been extensively investigated. This is due to a rich number of fascinating properties observed in materials containing small submicrometer clusters, which imply promising applications in various areas of nanotechnology [1]. Thin films of metal nanoparticles have been receiving increasing attention because of the optical, electronic, and catalytic properties of such materials [2].

Thin films palladium have been the focus of many studies because of their ability to separate hydrogen from other gases [3]. Furthermore Pd has remained a focus of the material science community due to its important band gap, conversion efficiency, high absorption coefficient, stability and there exists a vast literature covering theoretical and experimental studies of electronic band structure [4-6]. Pd has a wide and direct band gap, n-type semiconducting material and found in crystalline form fcc phase [2]. A number of deposition techniques are being used for the fabrication of Pd thin films including thermal evaporation, chemical bath deposition, vacuum evaporation, chemical vapour deposition, spray pyrolysis, metal organic vapour-phase epitaxy, closed space sublimation, photochemical deposition, radio frequency sputtering, vapour transport deposition electro deposition, screen printing , pulsed laser deposition and couting [7].

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2. Experimental

In this research program, palladium metal (99/95% pure) was purchased from goodfellow Co. Thin films of palladium were prepared by electron beam coating method on glass substrates using graphite crucible. Substrates were cleaned for about 5 min by ultrasonic cleaner. The system was pumped to a base pressure of less than 3×10^{-5} mbar before deposition. Other coating parameter were cathode voltage 8.5 kV, substrate temperature 32˚C, coating rate 12 $Å \cdot s^{-1}$. Film thickness was estimate to be about 123 Å. These films were then annealed in air at various temperatures ranging from 350˚C to 650˚C for a fixed time of 1 h.

The structure of these films was studied by X-ray diffraction (XRD) using Cu Kα (1.5418 Å) radiation with operating voltage/current of 40 kV. The optical property including optical band gap were calculated from the transmission spectra between 300 - 900 nm recorded by UV-Vis spectrometer.

In this research, Pd thin films have been coated by electron beam coating and their properties surveyed by UV-Vis spectrometer.

3. Results and Discussion

3.1. Structure Analysis

The structures of the Pd thin films were studied using X-ray diffraction (XRD) technique. The diffraction spec-

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tra were measured at 2θ scanning ranging from 0 to 90 degrees diffraction angle. The XRD spectra of Pd thin films with same thicknesses on glass substrates and annealed different temperature are shown in **Figure 1**.

These patters show that with increasing of temperature, intensity of obtained peaks increases. Intensities of reflections corresponding to the planes indifferent samples are different. However the strong reflections in all the samples indicates crystallites corresponding to (004) plane (2θ = 35˚) and (111) plane (2θ = 41˚). The calculated crystallite sizes of samples were found in the rang of 3 - 19 nm by applying the Scherrer formula. Generally the crystallite size depends on the annealing temperature [8].

3.2. Optical Analysis

The optical adsorption spectra annealed palladium films were recorded using a UV-visible spectrometer in the wave-length rang 300 - 900 nm. These spectra displayed in **Figure 2**.

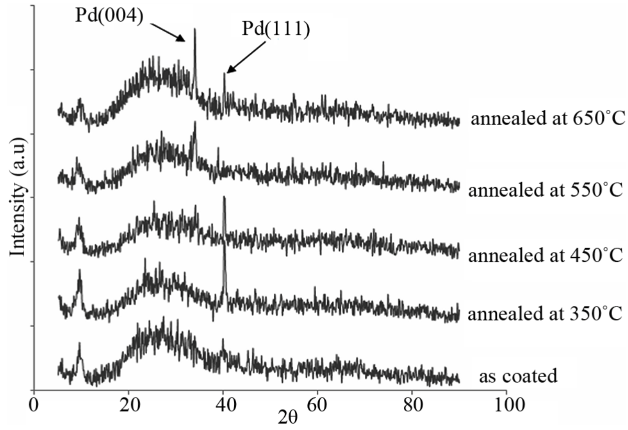

Figure 1. XRD spectra of Pd thin films.

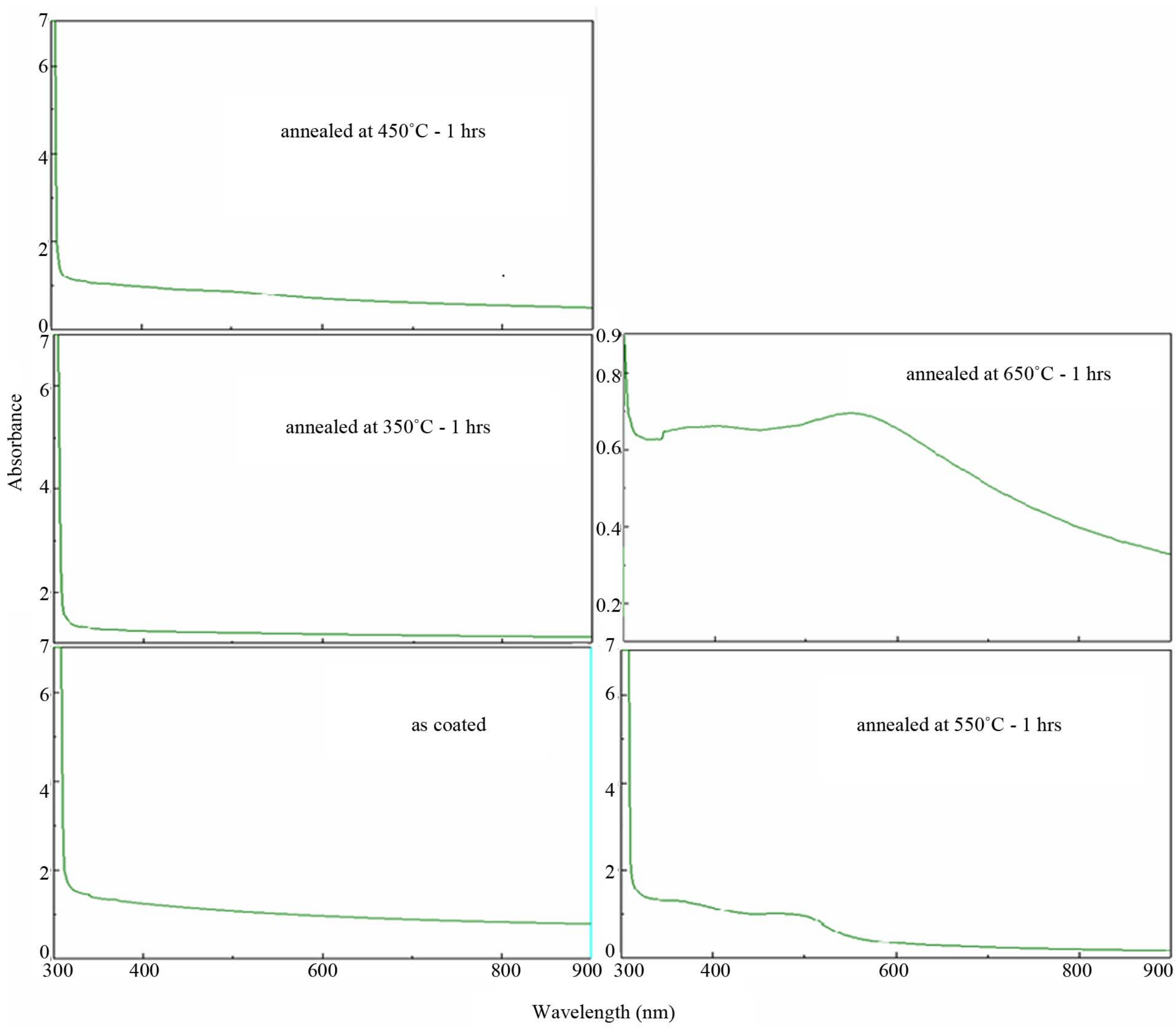

Figure 2. UV-visible spectra.

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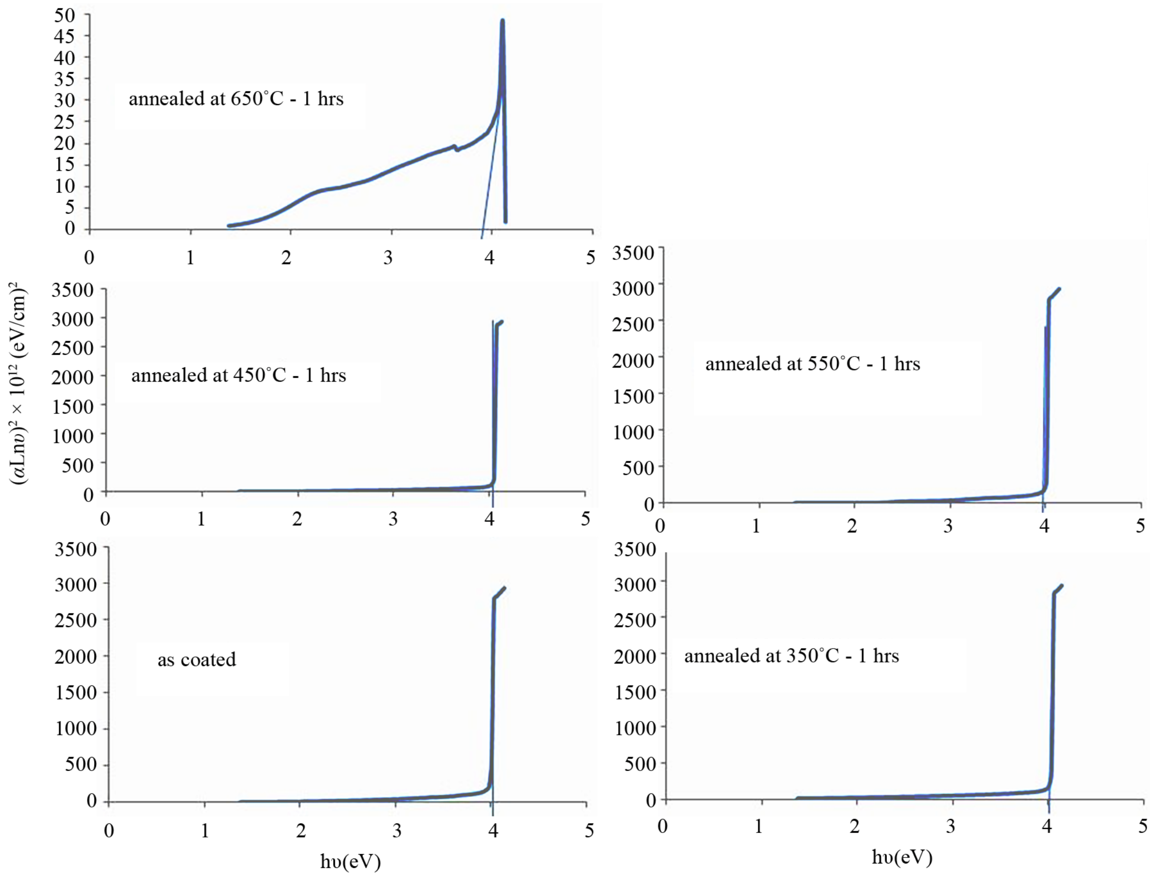

Figure 3. Plot of absorption coefficient, *α*, vs. photon energy (*hv*) of Pd thin films.

The optical absorption coefficient (α) was calculated from the absorbance (A). after correction for reflection losses α can be obtained using the following equation [9]:

$$\alpha(\nu) = 2.303\frac{A}{\mathrm{d}}$$

where d is the film thickness in cm and defined by $A = \mathrm{Log}(I/I_0)$ where I and I_0 are the intensities of the incident and transmitted beams, respectively.

The optical band gaps (E_g) of the films can be obtained according to its depence on α and energy hν of the incident photon, as expressed by following equation (Davis and Mott; 1970) [10,11]:

$$\alpha h\nu = B\left(h\nu - E_g\right)^n$$

where $h\nu$ is the energy of incidence photon, E_g is the value of the optical energy gap between the valence band and the the condition band, B is a constant that depends on the electronic transition probability and the exponent is a parameter which depends on the type of electronic transition responsible for absorption. Values of n = 2 and n = 1/2 correspond, respectively, to allowed indirect and allowed direct optical transitions [8,12,13].

The usual method for the determination of the value of E_g involves plotting $(\alpha h\nu)^{1/n}$ against ($h\nu$). In this study the most satisfactory results were obtained by plotting $(\alpha h\nu)^2$ as a function of the photon energy ($h\nu$). Such plots have been shown in **Figure 3**.

E_g, at various temperature were estimated by extrapolating the linear portion of $(\alpha h\nu)^2$. The optical band gap was shifted toward the lower energy from 4.1 to 3.87 eV as the annealing temperature rose from room temperature to 650˚C. These show that with increasing temperature, values of obtained band gap decreased.

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