Ellipsometry on optically thin palladium films on silicon-based substrate: effects of low concentration of hydrogen

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Abstract. Optically thin palladium films evaporated on silicon substrates are investigated following exposure to low concentrations of hydrogen gas in nitrogen using spectroscopic ellipsometry. Changes in the parameters tan Ψ and cos Δ are observed for concentrations as low as 0.01% hydrogen in nitrogen. A nonlinear behavior of the change in the ellipsometry parameters as a function of hydrogen concentration is demonstrated, with saturation occurring at a flow of 0.05% hydrogen in nitrogen. © *2005 Society of Photo-Optical Instrumentation Engineers.*
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1 Introduction

Hydrogen is considered the most likely candidate for a clean energy source of the 21st century. In view of that, a great deal of interest has developed over the past few decades in investigating the hydrogen-palladium system. This interest has risen from the use of palladium as a catalyst, which results from its ability to absorb up to 900 times its own volume in hydrogen. Hydrogen absorption results in structural changes in the metal through the formation of palladium hydride. This process is driven by surface adsorption, through chemisorption, followed by absorption through the palladium volume. One of the interesting characteristics in a hydrogen-palladium system is the transition from the α to β phase. Palladium is considered in the α phase when hydrogen is not present. However, with the introduction of hydrogen, the system passes through a mixed phase region and finally to a β phase.[1] The lattice constant changes as hydrogen enters the metal with a maximum change reaching 3% in the β phase. This process is reversible, thus, as the hydrogen is allowed to escape from the metal, the system returns to its original state.

In the past, most of the work in the hydrogen-palladium system has been for thick palladium films (in excess of 100 nm). Optically thick films experience a modification of their surface properties resulting from chemisorption, and hence a change in the Fresnel coefficients at the surface. This in turn leads to changes in reflectivity. Jansson et al.[2] have shown using ellipsometry that the optical properties of the surface of thick ~180-nm Pd films change on exposure to hydrogen and oxygen. They detected both reversible changes due to hydrogen exposure and irreversible changes related to the poisoning of the metal surface.

Although the bulk behavior of the palladium-hydrogen system is well characterized, very little work has been done for thin metal films of thickness less than a few tens of nanometers. Abnormal and interesting properties are expected at this film thickness, since outer surface effects and changes in optical thickness are complicated by the influence of the second boundary layer at the insulator-metal interface and by morphological changes of the optically thin metal. Any changes that may occur when exposing the palladium system to hydrogen gas are a combination of the surface effects (morphological changes) plus index of refraction changes of the bulk (which include thickness changes of palladium).

With the revolution of semiconductor technology and silicon-based integration of most devices, its important from both an application and fundamental point of view to investigate palladium metal films evaporated on silicon substrates. Even more important is to study optically thin metal films, which offer additional properties arising from structural changes on nanometer scales. Recently, we have used optical techniques to investigate the behavior of several optically thin palladium metal films evaporated on a silicon oxide substrate.[3–6]

Here we further investigate the exposure to hydrogen of palladium metal thin films evaporated on silicon-based substrates. Spectroscopic ellipsometry is used on various optically thin films of palladium evaporated on silicon dioxide/silicon substrates to study hydrogen effects on the films. Of particular interest are the changes observed as a function of wavelength following hydrogen exposure.

2 Experimental

The silicon wafers (*p*-type 5 ohms cm) were processed according to standard methods used to obtain gas sensitive catalytic metal-oxide-silicon devices.[7] The silicon dioxide wafers were oxidized in dry oxygen at 1100°C to a thickness of 150 nm. The process was followed by a 15-min anneal in argon at the same temperature. The palladium films were deposited by thermal evaporation at a background pressure of about 10^{-7} Torr, for a deposition rate of 2 to 3 Å per second. The samples were kept at room temperature during the evaporation, and no annealing of the films was performed before the measurements were made.

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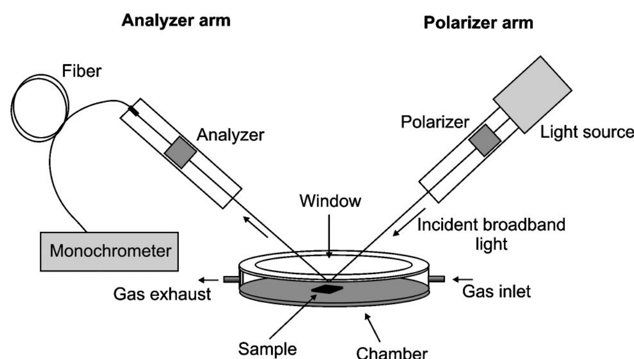

Fig. 1 A schematic diagram of a chamber for exposing the Pd samples to hydrogen gas and allowing spectroscopic ellipsometry measurements to be performed.

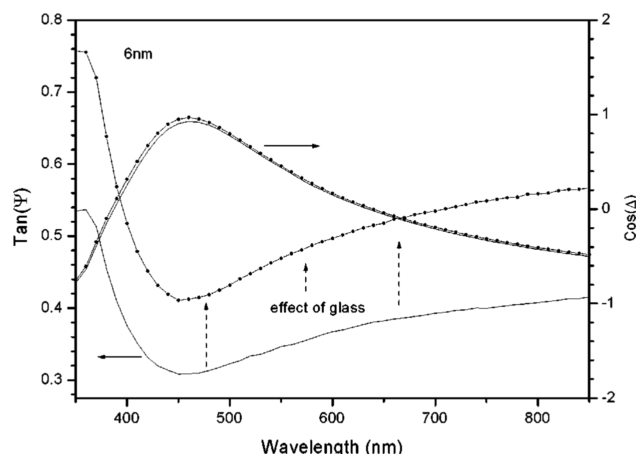

Fig. 2 Ellipsometry measurements showing the effects of the glass window of the chamber on the 6-nm Pd sample. The $\tan \Psi$ parameter shows a shift in its values, whereas the $\cos \Delta$ appears to be unchanged.

The spectroscopic ellipsometer used in these measurements is based on a rotating polarizer instrument with a white light source and a monochrometer at the end of the optical path for wavelength selection.

The broadband light coming from the polarizer arm was directed onto the Pd sample, which was within a specially designed chamber. The chamber was cylindrical in shape (6 cm diam and 1 cm height) equipped with suitable inlet and exhaust gas ports. The gas mixtures were provided by gas cylinders controlled by pressure regulators and subsequently with flow meters. The gases were mixed to give a homogeneous flow with a flow rate of 150 ml/min. The UV window of the chamber was 1 mm thick and 5 cm in diameter. The sample was placed approximately 1 mm from the end of the window, as seen in Fig. 1.

3 Results and Discussion

3.1 *Effect of the Glass Window*

In this work we have used several optically thick Pd films to measure and analyze the effect of hydrogen on the Pd/silicon system. Since the measurements were made on the samples placed in a chamber with a window, our first step was to remove the effect of the window from our results. This was accomplished by making measurements with and without the window present on the chamber. Figure 2 shows the results obtained for one of the Pd films, namely the 6-nm sample.

Clearly evident in the data is the effect of the glass on the $\tan \Psi$ parameter, where there is a simple shift in the values due to the index of refraction of the glass. The $\cos \Delta$ parameter is unaffected from the insertion of the glass. The effect of the window on our results is explained in more detail next. In the case where measurements were made with the window, the detected electric field by the ellipsometer may be described using the following expression[8]:

$$E_d = A \cdot R_A \cdot W \cdot S \cdot W \cdot R_P \cdot P \cdot E_s , \tag{1}$$

where A, R_A, W, S, R_P, P, and E_s represent the analyzer, the rotation associated with the analyzer, the window, the sample, the rotation associated to the polarizer, the polarizer, and the source, respectively.

The ellipsometry parameters $\tan \Psi$ and $\cos \Delta$ are defined by:

$$\tan \Psi = \frac{|r_p|}{|r_s|}, \quad \Delta = \delta_p - \delta_s , \tag{2}$$

where $r_p = |r_p| \exp(i\delta_p)$ and $r_s = |r_s| \exp(i\delta_s)$ represent the reflection coefficients with polarizations parallel and perpendicular to the plane of incidence. The difference between the ellipsometry parameters measured without (subscript wo) and with the window (subscript w) are given by:

$$\tan \Psi_{\mathrm{w}} = \left(\frac{|a|}{|b|} \right)^2 \tan \Psi_{\mathrm{wo}} ,$$
$$\cos \Delta_{\mathrm{w}} = \cos[\Delta_{\mathrm{wo}} - 2(\delta_a - \delta_b)], \tag{3}$$

where $a = |a| \exp(i\delta_a)$ and $b = |b| \exp(i\delta_b)$ represent the two transmission coefficients of the window in the plane and perpendicular to the plane of incidence, respectively. Since the phase shift due to the thickness of the window is identical, then $\delta_a - \delta_b = 0$, and we expect that $\cos \Delta_{\mathrm{w}} = \cos \Delta_{\mathrm{wo}}$, as seen from the measurements in Fig. 2. Using the ellipsometry measurements for each of the Pd samples with and without the window on the chamber, we were able to obtain correction factors for all the samples in this work. Here we should point out that there was no effect detected on the ellipsometry measurements when nitrogen was flowing in the chamber. Furthermore, there was no change in the ellipsometry parameters when only the substrate (silicon oxide/silicon) of the samples (Pd not present) was exposed to hydrogen.

3.2 *Ellipsometry Measurements in Optically Thin Pd Films*

During the exposure of a Pd sample to hydrogen, ellipsometry measurements were taken at continuous intervals to determine the point where the system reached equilibrium. For the samples used in this work and the hydrogen concentrations of interest, it appears that equilibrium was reached where the maximum change in the measurements occurred. Once a hydrogen exposure measurement was completed, the system was purged with nitrogen until we

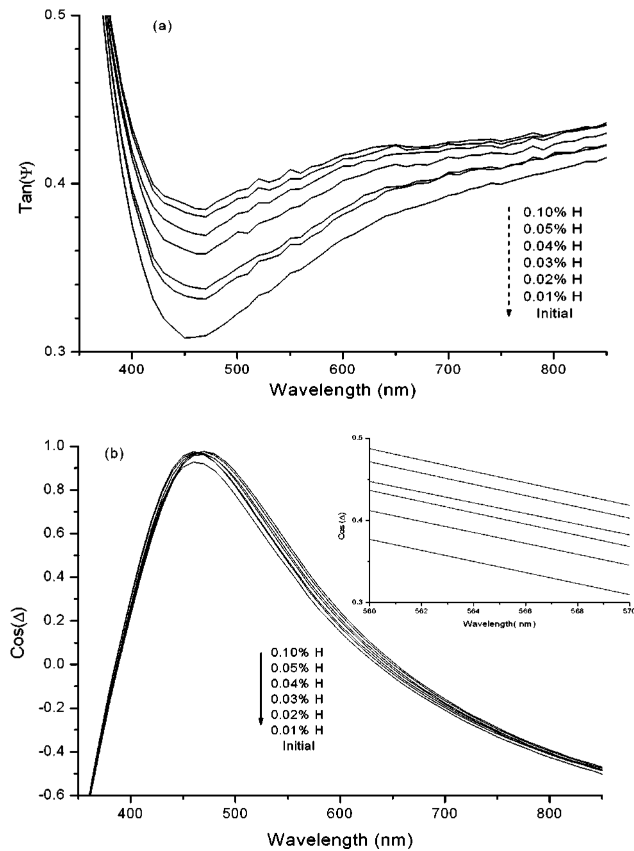

Fig. 3 Ellipsometry measurements for the 6-nm Pd film with the glass effect removed for various exposure concentration of hydrogen in nitrogen. The graph at the upper corner of (b) is the same graph plotted on the same *y* scale as (a) for comparison purposes.

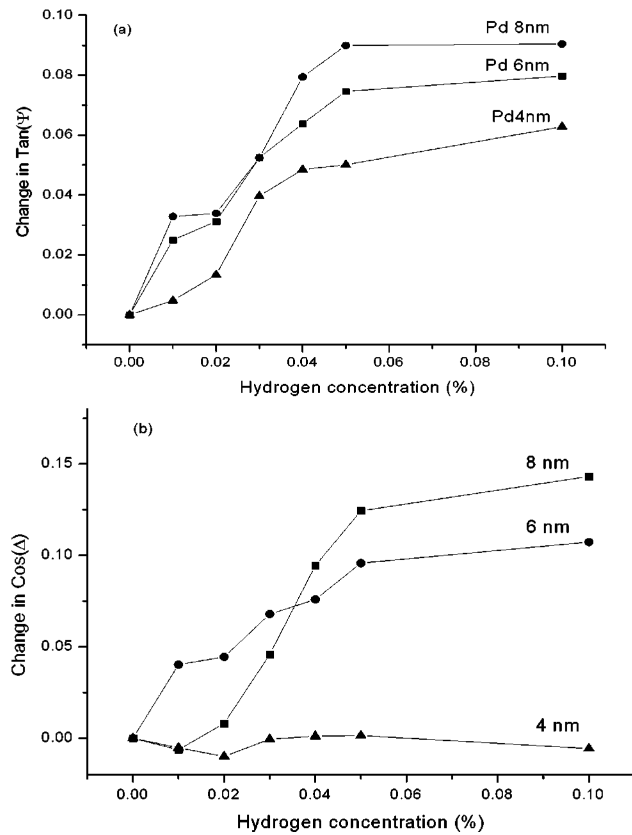

Fig. 4 Maximum changes in the $\tan\Psi$ and $\cos\Delta$ parameters from measurements for the 8-, 6-, and 4-nm Pd films as a function of hydrogen concentration flow in nitrogen.

confirmed the sample reached its initial state using the initial ellipsometry parameter values as a point of reference. The changes induced in the Pd samples due to their exposure to hydrogen appear to be completely reversible, as seen in other types of optical measurements on the same set of samples.[4–6] Using the determined window-correction factor, we were able to remove the glass effect from the ellipsometry measurements for the different exposure concentrations of hydrogen in nitrogen. Typical results for both ellipsometry parameters are shown in Figs. 3(a) and 3(b). Although it may not be obvious from Figs. 3(a) and 3(b) (due to the different scales), both ellipsometry parameters are changing as a function of the hydrogen concentration by similar values [see the upper right corner in Fig. 3(b)]. Furthermore, from the data we notice that the maximum changes occur in the spectra range of 450 to 600 nm with the incident angle set at 60 deg. Similar results have been observed with the 4-nm Pd sample. With decreasing thickness of the Pd film, it appears that the induced change in the ellipsometry parameters due to exposure of hydrogen decreases. This is evident for the 2-nm Pd film results, where the change in the $\tan\Psi$ parameter was barely noticeable for 0.1% H, the highest hydrogen concentration used in these experiments. Measurements for the thickest Pd sample (8 nm) have indicated a similar behavior, as in the other samples.

The penetration depth of Pd metal in the spectra range of 350 to 850 nm is approximately 10 to 12 nm. This implies that for the spectra range of interest in this work, the probing of the Pd samples occurs throughout its depth. For thinner samples, only a small fraction of the beam intensity probes the changes that occur in the Pd due to the hydrogen. Most of the energy will penetrate the Pd, where part of it will be reflected and part will be absorbed by the Si substrate. However, measurements on the silicon substrate have indicated that no change in the ellipsometry parameters is noticeable due to the presence of hydrogen. Therefore, although most of the reflected signal from the sample comes from the substrate, it will not contribute to changes in the ellipsometry parameters.

3.3 *Maximum Changes in Ellipsometry Parameters as a Function of Hydrogen Concentration*

In the final graphs, we display the maximum change in the $\tan\Psi$ and $\cos\Delta$ ellipsometry parameters as a function of hydrogen concentration for the various optically thin Pd films measured in this work. The first point to be made is that the maximum change occurs for the thicker samples. There is clearly a nonlinear behavior of the change in the ellipsometry parameters as a function of the hydrogen concentration, with saturation occurring around 0.05% hydrogen in nitrogen. The changes observed in both ellipsometry parameters from the exposure of the Pd film samples to hydrogen are believed to be due to changes in the index of refraction of the Pd as well as changes at the surface of the

metal.[4,5] However, as seen from the previous data (Fig. 4), the changes of the ellipsometry parameters increase with increasing thickness of the Pd metal sample. To a first approximation, we may assume that the surface contribution to the signal is constant with increasing thickness of the samples, since the surface area remains the same. This reasoning allows us to conclude that the major contribution to the change of the ellipsometry parameters comes from the changes in the ''bulk'' of the metal rather than the surface.

4 Conclusion

We investigate the effect of low concentration of hydrogen in optically thin Pd films evaporated on a silicon substrate using ellipsometry. We demonstrate the change of the $\tan\Psi$ and $\cos\Delta$ parameters in the range of 0.1 to 0.01% hydrogen in nitrogen. These samples exhibit a nonlinear behavior of the ellipsometry parameters as a function of hydrogen concentration with saturation occurring around 0.05% hydrogen in nitrogen. Finally, from simple extrapolation and the ratio of signal to noise in the data, changes in the ellipsometry parameters for the 8-nm Pd film can be detected as low as 0.001% hydrogen in nitrogen.

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