A Laser Beam Deflection System for Measuring Stress Variations in Thin Film Electrodes

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ABSTRACT

The bending beam method for measurements of stress in thin films deposited on an elastic substrate in the form of a thin stripe has been improved by the introduction of a laser beam deflection system and of a laser spot position detector. With this improvement, stress measurements have been performed *in situ* during the electrochemical reactions of palladium hydride formation and of valve metal anodic oxidation. Stress changes in the thin films of 10^7 N/m^2 can be measured with a time response better than 1s. This allows the detection of rapid reactions (like H diffusion in a Pd thin film) and of the electrostriction effect even in anodic films with thickness below 20 nm.

Cracking and peeling of thin metal or passive films can occur if high internal stresses build up, as in some cases due to an electrochemical reaction. Examples of measurements of internal stress have been given for electroplated films (1-5), as well as for vacuum-deposited metal films (6, 7), and considerable effort has been put in the detection of stresses developed during oxidation of bulk metals and metal films (8-16). This shows that the measurement of such stresses, and the knowledge of how they develop into the films during a reaction, is still of considerable importance for several industrial applications where protective coatings are obtained by an electrochemical method. A reliable stress measurement technique should therefore be simple, *in situ*, sensitive, and fast. The first quantitative measurements of stress in thin electroplated films were carried out by Mills (1) and by Stoney (2). Stoney measured the bending of a sample in the form of a long, thin, rectangular steel rule which was clamped at one end and had one side lacquered. More recent measurements of stress in the anodic films of various metals have followed the same procedure, making use of a telescope or of a traveling vernier microscope to measure the specimens' deflections (8, 16). Other different methods of stress measurements are optical, interferometric, electrical or electromechanical, and by x-ray or electron diffraction (6, 18). A very sensitive interferometric *in situ* technique for measuring electrode strain has been recently proposed by Butler and Ginley (5, 19) taking a single-mode optical fiber as the thin film electrode substrate.

In the present work, we use once more the old bending beam method of Stoney, but we improve its design taking a laser and a position sensitive detector to improve both the sensitivity and the response time. This results in a simple but precise electro-optical setup for *in situ* measurements, that could easily be automated and used routinely in industrial laboratories. In a recent, short note (20) we described this setup and discussed briefly its application for studying stress changes in thin film during an electrochemical reaction. The applicability of our setup has been shown in the present paper for two different electrochemical reactions: the anodization of a thin valve metal film, and the cathodic formation of palladium hydride from a Pd film electrode. Other electrochemical reactions have also been investigated lately by us with the same setup, namely, the hydrogen electrochemical doping of various TiO$_2$ semiconducting film photoelectrodes, and the electrochromic reaction of nickel oxi-hydroxide films for smart windows applications, but these results will be reported elsewhere. It is now our conviction that a large number of electrochemical reactions induce internal stresses in a thin film electrode, and several physical phenomena can be responsible for the stress: thermal expansion, electrocapillarity, diffusion or intercalation of species in the film, surface chemical and morphological modifications, electrical field effects. It is therefore the aim of this paper to study in some detail simple electrochemical reactions, already well known in electrochemistry, and to compare our experimental results with the stress calculated from the mechanical and electrical properties of the thin film materials.

Experimental Details

The experimental setup has already been described in a short report (20), and is shown in Fig. 1. An optical bench similar to that of Charbonnier *et al.* (21) has been modified in order to direct the He-Ne laser beam reflected from the lower end of the electrode on a linear position sensitive detector (UDT Model LSC/5D or Model LSC/30D), with its axis in the vertical direction. The working electrodes are thin metal films (0.1 μm thick) sputtered onto cover glass substrates (0.15 mm thick) prepared typically in the form of 3 × 30 mm rectangles, clamped by the upper end above the electrolyte level. The laser beam is reflected by the electrolyte/glass and (much more) by the glass/metal interface (this to avoid the disturbance due to reaction products and convective flows in front of the film) and falls onto the position cell, which senses the movement of the spot associated with the bending of the electrode. Two output photocurrents are generated which are proportional to the distance of the spot from the end contacts of the detector, thus providing real-time analog information on both position and movement of the spot. The bending of the electrode can be related to the stress in the thin film (Fig. 1B), provided the deflection angle $\Delta\theta$ and the radius of curvature R are measured and the mechanical and geometrical parameters of film and glass are known.

During our experiments, compressive stresses induced an upward, and tensile a downward deflection of the laser beam. The electronical equipment used here were a homemade double current-to-voltage converter, a differential amplifier (or a lock-in amplifier operating in its differential mode), to measure the deflection angle, and a conventional electrochemical setup (PAR 173 potentiostat galvanostat and PAR 175 programmer) to control either the potential (with respect to a saturated calomel reference electrode, SCE) or the current in the electrochemical cell. The electrolytes were prepared from AnalaR grade reagents in triply distilled water, purged with N$_2$, when necessary, and measurements were performed at room temperature. The laser deflection due to thermal expansion of the electrode has been calculated to be of 10^{-5} rad/°K, thus smaller than the deflections we measured experimentally, and therefore the electrochemical cell was not kept under thermostatic control. The heating of the film electrode due to the laser beam probe (less than 0.5 mW after beam splitting) was also considered to be negligible, under the present circumstances.

Results

Electrochemical PdH$_x$ formation.—It is well known that atomic hydrogen can easily diffuse into palladium (23), this property having been used for hydrogen storage and hydrogen sensors (23, 24), among other applications. Since at room temperature the diffusion coefficient of H in Pd is of 3×10^{-7} cm^2/s (25), the H diffusion throughout a Pd film
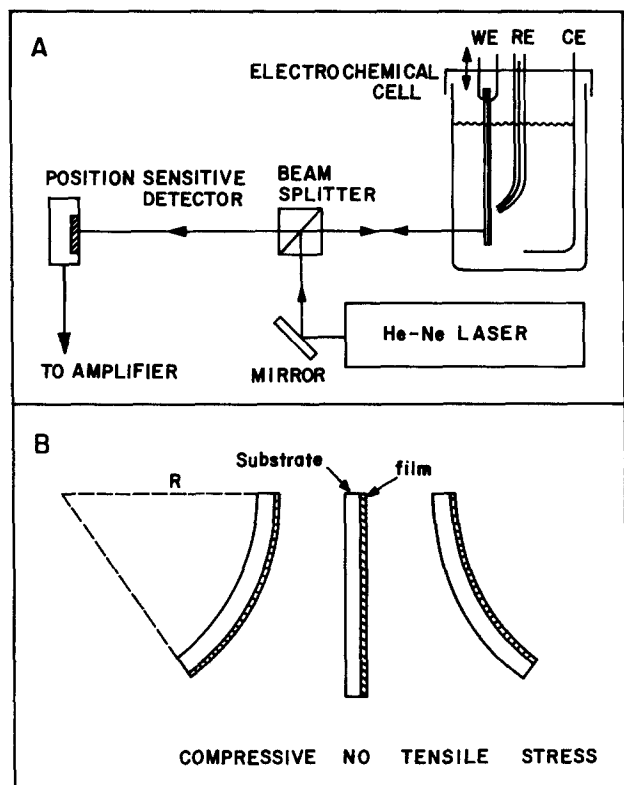
Fig. 1. (A) Experimental setup used for measuring stress in a thin film during electrochemical reactions; WE, RE, and CE are the working, calomel reference, and counterelectrodes, respectively. (B) Bending of a long, thin substrate due to compressive or tensile stress in the thin film (side view). Δθ: deflection angle. R: radius of curvature.
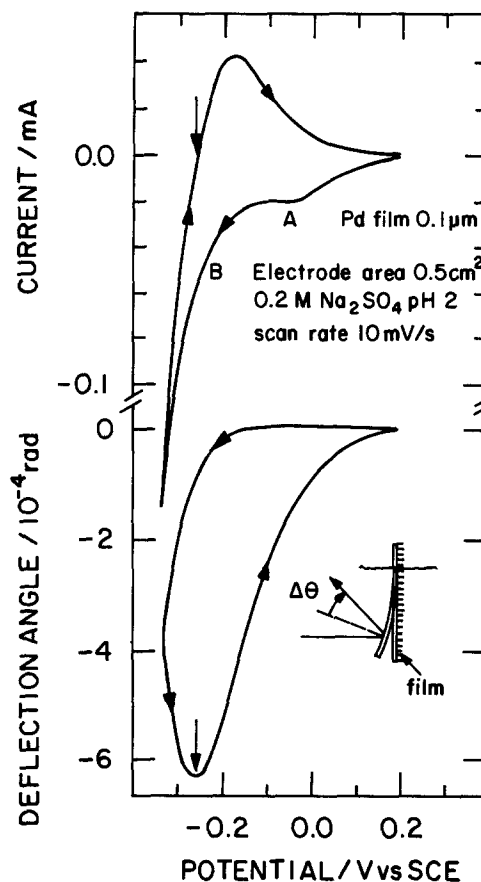

Fig. 2. Cyclic voltammogram (upper curve) and simultaneous variation of the deflection angle Δθ (lower curve) with a thin Pd film electrode in air saturated Na_2SO_4 electrolyte.

0.1 μm thick occurs in less than 10^{-3}s. We have performed several experiments in which hydrogen was generated electrochemically at a Pd film electrode surface, and in view of the above we have always assumed that on our time scale (of the order of seconds) most of the H atoms generated diffuse into the film and the measured deflection is the effect of stress due to a uniform, homogeneous solid solution of H in Pd (denominated PdH_x). The validity of this assumption will be discussed later. In Fig. 2 the cyclic voltammogram of such a Pd film electrode is shown, together with the simultaneous measurement of the deflection angle of the probe laser beam. Two reactions are observed on the cathodic scan: reaction A, associated with the reduction of O_2 dissolved in the (air-saturated) electrolyte, and with no effect on the laser beam deflection; and reaction B, that we could tentatively write as

$$Pd + xH^+ + xe^- \rightarrow PdH_x \qquad [1]$$

which is accompanied by a sizable deflection indicating increasing compressive stress into the film as the reaction proceeds. By convention, this kind of deflection will be measured with negative angles, while for the deflection associated with increasing tensile stress positive angles will be used. On the reverse scan, the potential of maximum deflection has been marked in Fig. 2 with an arrow, and corresponds to the point of zero current in the voltammogram. Following the stripping reaction of H^+ (the reverse of Eq. [1]) both the current and the deflection angle go back to their initial value, and the cycle can be reproduced. In Fig. 3 the deflection angles are shown as a function of time, when galvanostatic experiments are started with a similar Pd electrode in the same electrolyte at time $t = 0$. When the deflection angles are plotted as a function of charge (inset of Fig. 3), only the results obtained with the higher currents densities are very close to each other. This can be explained as if these currents were larger than the limiting current of O_2 reduction under natural convection (no stirring) of the electrolyte. With $|J|$ smaller than 50 μA/cm², instead, a considerable fraction of the charge passed should therefore be associated with the oxygen reduction

reaction and not with the hydrogen generation. The experiment with $J = -66$ μA/cm² shows also at $t = 55$s the effect of stopping the galvanostatic experiment on the deflection angle, where the release of stress suggests a spontaneous diffusion of hydrogen out of the film. This effect was only observed in air-saturated electrolytes. The experiment with $J = -55$ μA/cm² has been prolonged till the destruction of the specimen which occurred due to the peeling of the film from its substrate.
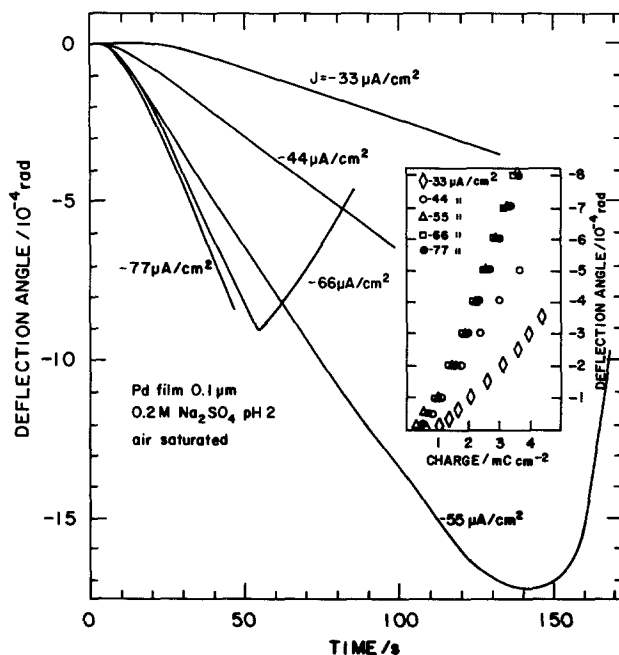

Fig. 3. Time dependence of the deflection angle Δθ during galvanostatic experiments with a Pd film electrode. Electrolyte as in Fig. 2.

In order to avoid the reduction of O_2, that has no effect on the stress in the thin film electrode, we have saturated the cell electrolyte with nitrogen and repeated a series of galvanostatic experiments. The results in Fig. 4 show that the deflection angles are larger than those in the experiments in Fig. 3, and that there is a single linear relationship between deflection angles and charge (inset of Fig. 4), regardless of the current density. In the experiment with $J = -47$ µA/cm^2 two points can be marked on the curve: A is the proportionality limit, below which the deflection is linearly proportional to the charge, and B is the rupture point, where the peeling of the film begins to occur. The results shown in Fig. 4 have been reproduced with other Pd thin film specimens. Nb thin film electrodes have also been investigated under similar experimental conditions, and a linear relationship (with different slope) has been observed between deflection angle and charge as well.

Anodic oxidation of thin metal films.—Stresses in anodic films (18) arise because of the displacement of metal and oxygen ions during anodization, because of the changes in volume and in porosity of the surface layer (15), and also as a consequence of the high electric field (electrostriction). We have investigated the stress in the anodic oxides produced by cyclic voltammetry in the potential range up to 10V on thin Nb and Ti films. The laser beam deflection during the anodization of a niobium film (Fig. 5, curve 1) indicates tensile stress which develops already in the potential region between 1 and 3V (corresponding to oxide film thickness of about 5 nm), and only on the first cycle. Subsequent cycles (Fig. 5, curve 2), even when extended to higher potentials (Fig. 5, curve 3), do not change the deflection developed below 3V, apart from a small decrease of the deflection angle observed with the voltage applied, which can be explained as compressive electrostriction. This field effect is only -3×10^{-5} rad at 10V, compared to $+1.8 \times 10^{-4}$ rad developed on the first anodic voltammetry.

The results obtained with a Ti thin film electrode again indicate that tensile stress develops only during the first cycle (Fig. 6, curve 1), but point out (Fig. 6, curve 3) a much larger compressive effect due to the electric field (-1.4×10^{-4} rad at 10V). It should also be noticed that we always observed larger and increasing currents during the first anodic potential sweep on Ti film electrodes than on Nb. This could be due to the oxygen side reaction on Ti or to the transpassivity and instability of its oxide. As a result, the tensile stress in the titanium oxide requires higher
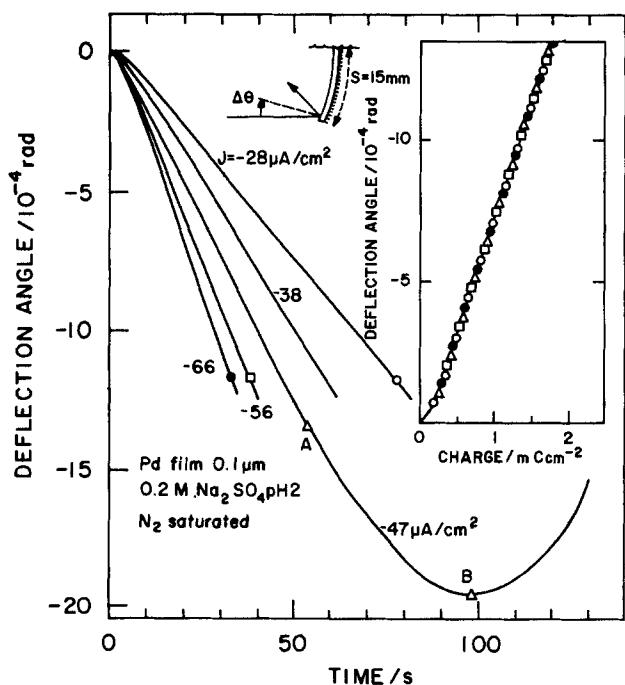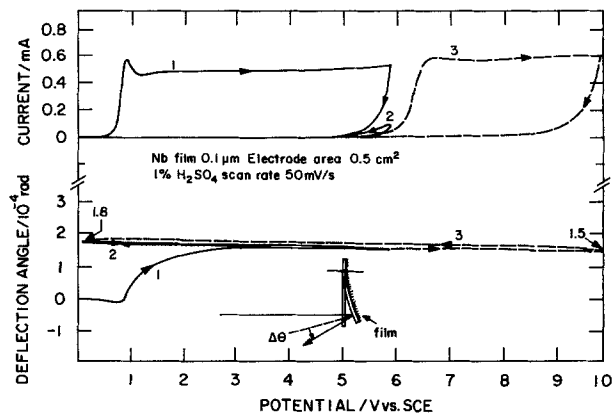

Fig. 5. Cyclic voltammograms (upper curves) and simultaneous variation of the deflection angle $\Delta\theta$ (lower curves) with a Nb film electrode in H_2SO_4 electrolyte.

voltages and/or more time to fully develop than the one in the niobium oxide films. Only during the second and subsequent voltammetric cycles with Ti film electrodes one can observe in the deflection angles the characteristic behavior of a stabilized oxide, *i.e.*, an angular decrease as a function of increasing applied voltage.

Discussion

In the so-called bending beam method, the measurements of stress require that the substrate is at least five times longer than it is broad and the sensitivity depends on the detection system used to observe the displacement of one end of the specimen while the other is clamped (18). The detection system used in the present paper allowed the measurement of a minimum deflection angle of the probe laser beam of 5×10^{-6} rad, that corresponds to a movement of 5×10^{-5} mm of the free end of a 20 mm long electrode. Such a small displacement could not be measured by any of the optical systems described so far based on the visual observation of the free lower end of the electrode during an electrochemical reaction (2, 8, 16), and could be detected optically only by an interferometric method. Furthermore, the maximum sensitivity of the present technique could still be enhanced, since it has been proven that much smaller laser beam deflection angles can be detected in mirage experiments with a similar optical setup (21).

The formula we used for calculating stress in terms of the radius of curvature R of the substrate has been derived already by Stoney (2) and modified later (18) by the introduction of Poisson's ratio of the substrate ν

Fig. 4. Time dependence of the deflection angle $\Delta\theta$ during galvanostatic experiments with a Pd film electrode in N_2-saturated Na_2SO_4 electrolyte.
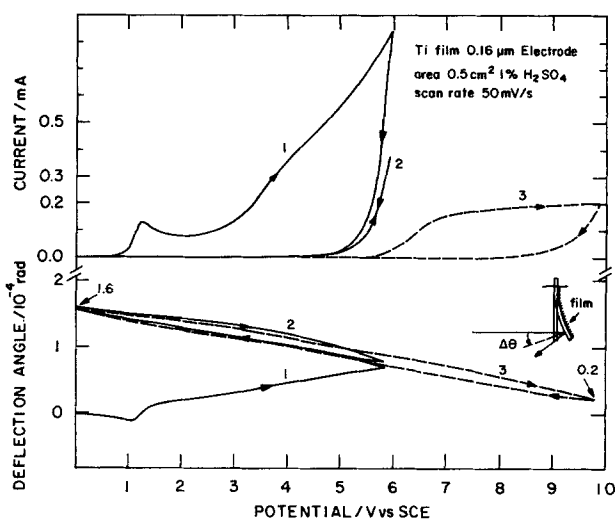

Fig. 6. Cyclic voltammograms (upper curves) and simultaneous variation of the deflection angle $\Delta\theta$ (lower curves) with a Ti film electrode in H_2SO_4 electrolyte.

$$\sigma = \frac{E}{6\,(1-\nu)} \cdot \frac{t^2}{t_f} \cdot \frac{1}{R} \quad \text{with } R = \frac{s}{\Delta\theta} \qquad [2]$$

where E is the substrate Young's modulus, t and t_f the substrate and film thickness, respectively, s the length of the sample (in our case, the distance between the laser beam spot on the electrode and the electrolyte meniscus) and $\Delta\theta$ the measured deflection. If the film under study is already stressed, prior to the electrochemical reaction, Eq. [2] gives the stress variation due to the reaction only. For absolute stress determination, one should measure first the radius of curvature of the substrate alone R_1, then the radius of curvature R_2 of the substrate with film. The absolute stress in the thin film can therefore be calculated as follows (26)

$$\sigma = \frac{E}{6\,(1-\nu)} \cdot \frac{t^2}{t_f} \cdot \left(\frac{1}{R_2} - \frac{1}{R_1} \right) \qquad [3]$$

Since the discussion of our results will be restricted to the analysis of stress variations due to the electrochemical reactions, we shall only use Eq. [2] in the following.

The results shown in the Fig. 2-4 can be explained in terms of a compressive stress associated with a volume increase of the thin metal film during the cathodic reduction reaction of the protons of the electrolyte (Eq. [1]). The lattice expansion has been studied in detail for several bulk metal-hydrogen systems (27), and the relative volume change $(\Delta V/\Omega)$ per unit concentration of H in Pd has been found to be 0.19. For a Pd metal in the form of a long bar that has both ends blocked, one can therefore calculate the stress per unit concentration of H in the simple way

$$\sigma_{calc} = \frac{E_m}{1-\nu_m} \frac{\Delta L}{L} = \frac{E_m}{1-\nu_m} \frac{1}{3} \frac{\Delta V}{\Omega} = 1.22 \times 10^{10}\ \text{N/m}^2 \quad [4]$$

taking $E_m = 1.17 \times 10^{11}\ \text{N/m}^2$ and $\nu_m = 0.39$ (28), where the subscript m indicates metal. We compare this calculated value with the experimental stress derived from Fig. 4 by means of Eq. [2]. This comparison is possible only if the linear expansion of the film attached to the glass substrate is very small. This is indeed the case here, because the film expansion due to the bending of the glass substrate is only 0.4% of that of a free unsupported metal bar of the same length charged with the same H concentration. From the slope of the straight line in the inset of Fig. 4 (5.73×10^{-5} rad m²/C), and taking for the glass substrate the following constants $E = 7.0 \times 10^{10}\ \text{N/m}^2$, $\nu = 0.22$, $t = 1.5 \times 10^{-4}$m, the stress after passing a charge of 1 C/m² in a 0.1 μm thick Pd film is $1.29 \times 10^7\ \text{N/m}^2$. Since from Faraday's law one needs 1.088×10^3 C/m² to get a unit concentration of H in a 0.1 μm thick Pd film (assuming no evolution of gaseous H_2 at the Pd electrode), the experimental stress per unit concentration of H in Pd from the results in Fig. 4 is then 1.40×10^{10} N/m² (*i.e.*, within 15% of the calculated value). The agreement between experimental and calculated values of the stress is better if we take the average value of sixteen measurements on five different Pd specimens (all in N_2 saturated electrolytes), which is $(1.12 \pm 0.7) \times 10^7$ N/m² after passing a charge of 1 C/m². The results of the experiments in air-saturated electrolytes (Fig. 2 and 3) cannot be compared with the former ones because in this case Faraday's law cannot be applied unless the exact faradaic efficiency of the reaction in Eq. [1] is known. The linear behavior shown by the deflection experiments like the ones in Fig. 4 and the agreement found above between experimental and calculated stress in the thin film PdH$_x$ electrodes support the following conclusions:

1. The assumption of uniform distribution of H in the PdH$_x$ film during our experiments appears justified.

2. The amount of gaseous H_2 evolved at the PdH$_x$ film electrode is negligible for small current densities (below 70 μA/cm²), since most of the H atoms generated were observed to diffuse into the film contributing to the measured stress.

3. The mechanical properties of the thin films of Pd described in this work seem to be very similar to those of the bulk metal material.

4. The compressive stress in the thin PdH$_x$ films can be measured *in situ* by means of the deflection angle of a laser beam and is in agreement with the lattice strain model. The stress is linearly proportional to the H concentration x, and is reversible if the elasticity limit of the specimen is not exceeded. With this respect, the proportionality limit $(x \simeq 3\%)$ and the rupture point $(x \simeq 4\%)$ appear to be mainly determined in our case by the adhesion between substrate and film, rather than by the mechanical properties of the film itself.

A completely different physical phenomena is the one related to the experiments described in Fig. 5 and 6. As already pointed out in the former section, the growth of a second layer (the anodic oxide) on top of the metal film generates, first, a tensile stress, which is permanent and nonreversible, and second, a compressive stress (electrostriction), which is only due to the electric field and is therefore reversible. For multilayer film structures the simple model from which Eq. [2] was derived would not be correct, but still could be used to calculate the stress variations due to the electric field forces, because these apply only to the outer dielectric layer, their net effect being to squeeze the oxide film without applying any stress on the underlying glass + metal film structure. Using the growth law for determining the oxide film thickness (2.1 nm/V for Nb_2O_5 and 2.0 nm/V for TiO_2) and taking the same glass substrate coefficients as above, one can deduce from the deflection angles in Fig. 5 and 6, being $s = 13$ mm, a compressive electrostriction at 10V of 3.7×10^7 N/m² for the niobium oxide and 1.9×10^8 N/m² for the titanium oxide. These experimental values can be compared with the stress in the oxide layer calculated by the attraction of two oppositely charged plates of a simple parallel plate capacitor, where the underlying metal layer is one electrode and the electrolyte is the other. This resulting stress is (19)

$$\sigma = \left| \frac{\nu}{1-\nu} \right| \cdot \frac{\epsilon\epsilon_o V^2}{2\,t_f^2} \qquad [5]$$

where ϵ_o is the permittivity of free space, ϵ the relative permittivity of Nb_2O_5 (40) and of TiO_2 (100), and V the applied voltage (10V). The calculated values of this stress are 2.7×10^7 and 7.4×10^7 N/m², for the niobium oxide and titanium oxide film 21 and 20 nm thick, respectively. The agreement between the experimental and calculated stress is better for Nb_2O_5 than for TiO_2. The larger electrostrictive effect measured for TiO_2 is related to its higher permittivity, but it is doubtful whether it is correct to consider the relative permittivity of thin anodic layers the same as that of bulk metal oxides, as done in the present calculations, and not to take into account the stress dependence of the permittivity (13). Different values of ϵ have been taken in the literature for explaining impedance and ellipsometrical measurements on thin films of TiO_2 (29) and Nb_2O_5 (30), but these values too were given with considerable uncertainty. Literature data report electrostrictive stresses measured experimentally of 2×10^7 N/m² in Nb_2O_5 (8) and between 1×10^8 N/m² (8) and 2×10^{18} N/m² (16) in TiO_2 (thus similar to our results), the latter being however a function of the anodizing time at fixed applied voltage.

Finally, we discuss briefly the tensile stress observed during the first anodization cycle of the thin metal electrode. This is a salient feature already observed elsewhere for all anodic oxides at small film thicknesses (8), and explained as due to progressive film dehydration, but its magnitude is often dependent upon the anodizing conditions. Our experiments allow one to follow continuously the buildup of this tensile stress in time, and therefore show that a steady-state value of tension is attained much earlier in Nb_2O_5 than in TiO_2, in agreement with the previous reports of instability of titanium oxide films (29, 16). Other authors also reported open-circuit tensile stress to be a function of the composition of the electrolyte in which the titanium oxide is grown as well as of the metal surface preparation (12). Unfortunately, for the sake of comparison, analogous experiments on the anodic oxides of niobium were not reported in the literature, to the best of our knowledge. In view of the dynamic conditions in which our deflection experiments were performed, and of the

lack of a more complete model for stress derivation in multilayer film structures, no attempt was made here to calculate quantitatively the tensile stress observed during the first anodization cycles of our Nb and Ti film electrodes. We believe, however, that the results of such laser beam deflection experiments can be useful for comparing the growth process of different anodic oxides and could be easily extended to the study *in situ* of a variety of anodizing conditions of the same metal electrode.

Conclusions

In this work measurements of stress variations in thin film electrodes have been performed *in situ* with a new electro-optic technique based on the bending beam method already developed by Stoney (2). This technique is fast and almost as sensitive as an interferometric technique, but it is simpler and requires cheaper components. With this technique we have studied the stress dependence on the hydrogen concentration x in PdH_x thin films in the range $0.001 < x < 0.04$ and found a very good agreement with the stress expected in a bulk PdH_x metal sample from the lattice strain model. The increase in compressive stress in the thin film can be determined precisely knowing the charge of the cathodic reaction, provided care is taken to avoid side reactions, a low reaction rate is kept, and the proportionality and rupture point of the film are not exceeded. The anodic oxidation of thin valve metal films (Nb and Ti) has also been studied here with this new technique, and the compressive stress due to the application of an electric field across the anodic films (electrostriction) has been analyzed. The measured electrostriction for Nb_2O_5 is in reasonable agreement with the calculated electrostriction and with literature data; for TiO_2 the measured electrostriction is larger than the electrostriction calculated taking into account the known permittivity of bulk titanium dioxide. Tensile stress has also been observed to develop during the first anodic potential excursion of both Nb and Ti thin film electrodes, but no conclusive explanation has been found for this effect yet. The technique reported here can easily be extended to the analysis of electrochemical reaction at thin metal foils, provided one side of the foil is lacquered and a small size optical mirror is attached to its lower end. The use of various substrate materials with different mechanical and thermal properties may result in higher sensitivity and in various applications of this technique. Further work is in progress and new results will be reported elsewhere.

Acknowledgments

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