

Quantitative optical recognition of highly reproducible ultrathin oxide films in microelectrochemical anodization

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Automatized microelectrochemical investigations are achieved using a scanning droplet cell. The area reproducibility for a 100 μm oxide spot is found to be better than 1%, a value typically difficult to reach even in macroscopic samples. A systematic change in color appearance is seen for oxide films with a thickness ranging from 14 to 27 nm. Analysis of optical images yields a strictly linear relation between relative transmission and anodization charge and thus allows determination of the oxide thickness with a remarkable precision better than 0.5 nm at an absolute film thickness value that is at least a factor of 20 smaller than the wavelength of light. © 2009 American Institute of Physics. [DOI: 10.1063/1.3117210]

In the last years, the instruments and methods for high throughput experimentation received increased interest,¹ and in particular were successfully used for electrochemical investigations.² The rapidly rising interest in electrochemical experimentation and more specific in microelectrochemistry in various fields such as batteries, corrosion, electroanalysis, electrocatalysis, fuel cells, and sensing is driving the development. The key for efficiently performing the experiments of interest is a powerful instrumentation. This can be realized either by multiplexed arrays,³ or by scanning systems, e.g., electrochemical robotic systems. The advantage of the latter is their versatility that can easily adapt to new requests.⁴ Optical and mechanical characterization techniques are already available for thin film composition spreads.^{5,6} Such a spread is typically smaller than 50 at. % on a 10 cm wafer. A spatial resolution of 200 μm for an electrochemical method thus yields a composition resolution of better than 0.1 at. %. This diameter is a good compromise of surface area in terms of signal/noise ratio and resolution when investigating highly Ohmic valve metal oxides (Al, Hf, Nb, Ta, Ti, and Zr) of the barrier type.

A sputtered high purity Hf thin film (99.995%) was used as substrate for localized microelectrochemical anodizations in acetate buffer and their subsequent optical analysis. A thermally oxidized Si wafer was used as substrate for the sputtering deposition in radio frequency (rf) mode with a sputtering rate of 0.96 nm s^{-1} . The deposition was carried out at room temperature (25.1 °C) in Ar atmosphere (6.66×10^{-1} Pa). The target-substrate distance was approximately 19 cm assuring the formation of a uniform thin film, 300 nm thick. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) microstructure analysis of the Hf sample (not shown here) revealed a superficial compact structure with metallic grains of approximately 100 nm in diameter and a surface roughness of 3.8 nm. X-ray diffraction crystallographic investigations indicated a polycrystalline structure of hexagonal symmetry.

The Hf thin film was locally anodized using a scanning droplet cell (SDC), where a small droplet of electrolyte hanging at the tip of a glass capillary comes in contact with the investigated sample thereby defining the working electrode (WE).⁷ An improved design of the SDC, which comprises an agar-suspended capillary-based μ -reference electrode inserted in the main capillary of the cell, was used.⁸ The outer diameter of the SDC capillary was defined by grinding the tip until approximately 200 μm were measured by an optical microscope. The electrical contact with the Hf thin film WE is provided using a W needle in hard contact with the sample.

The SDC was operated in the confined droplet mode,⁹ where the tip of the cell is brought in contact with the surface of the WE, thus confining the electrolyte droplet inside the capillary. For ensuring a perfect sealing of the electrolyte from the environment, a silicone microgasket was formed at the SDC tip. An elastic deformation of the silicone gasket was ensured using a sufficiently small contact force (2 mN) controlled by a force sensor. Self-made LABVIEW© software was used for controlling the movement of the SDC to certain predefined positions, the approach to the WE, the electrolyte volume at the tip, and all the electrochemical measurements. A previous version of the automated SDC system, operating in the free droplet mode, was described elsewhere.¹⁰

A 10×12 matrix of anodic oxide spots was grown on the surface of the Hf thin film using the automated SDC in the confined droplet mode. An optical image of these spots is shown in Fig. 1 under the illumination of a white light broad spectrum lamp. The oxide spots matrix has equipotential columns and a potential gradient was applied along the rows, the anodizing potential increasing from left to right. All the oxide spots were grown potentiostatically for 30 s at potentials ranging from 4.5 V (SHE) to 10 V (SHE) with a 0.5 V potential step between consecutive columns. Each following line is shifted by 31 μm resulting in an angle of 95° between rows and lines. The anodic oxide thicknesses were increased proportional to the charge consumed, according to Faraday's law, and the growth took place with a maximum current

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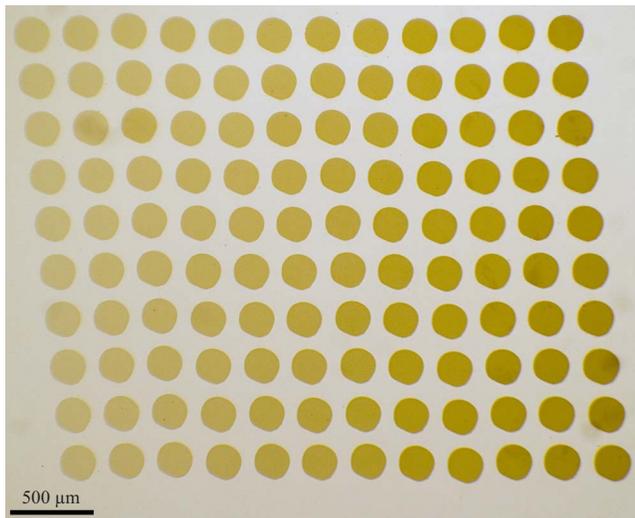


FIG. 1. (Color online) Optical microscope image of an array of oxide spots potentiostatically grown on Hf at various anodization potentials using the automated SDC.

efficiency, without side reactions, obeying the high field regime characteristic to valve metal anodizations.¹¹ Potentiodynamic anodizations on the same sample have shown a current density plateau corresponding to an oxide formation factor of 2.3 nm V^{-1} , confirming results obtained from previous studies.¹²

A quarter of the total amount of oxide spots, uniformly distributed along the matrix, was individually imaged at higher magnifications than the one in Fig. 1, the images having a resolution of 0.5 μm pix^{-1} . After the conversion of the optical image of each spot into a gray-scale representation, a threshold flooding algorithm was used with subsequent counting of the image pixels residing inside each oxide spot. The area of each oxide spot was calculated and the result is shown in Fig. 2. The area as determined from counting the pixels was converted into an ideally circular geometry and the resulting equivalent radius of each oxide spot was calculated. An average wetted area of $3.495 \times 10^{-4} \text{ cm}^2$ was measured and a deviation of only $\pm 0.5 \text{ μm}$, corresponding to an error of less than 1%, could be observed for the radius of the oxide spots. This proves the high reproducibility of the wetted surface area with the automated SDC and demonstrates

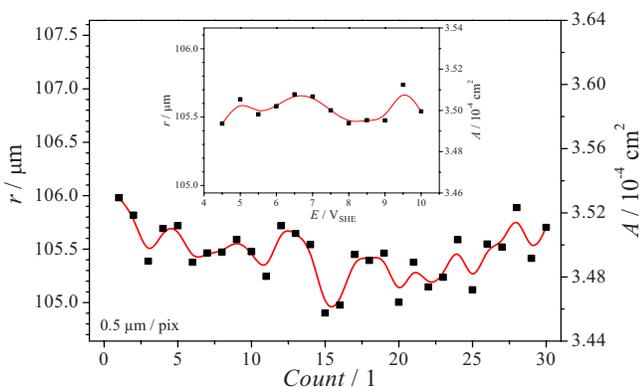


FIG. 2. (Color online) Areas and radiuses of oxide spots grown on Hf. Oxide spots areas distribution as a function of applied potential.

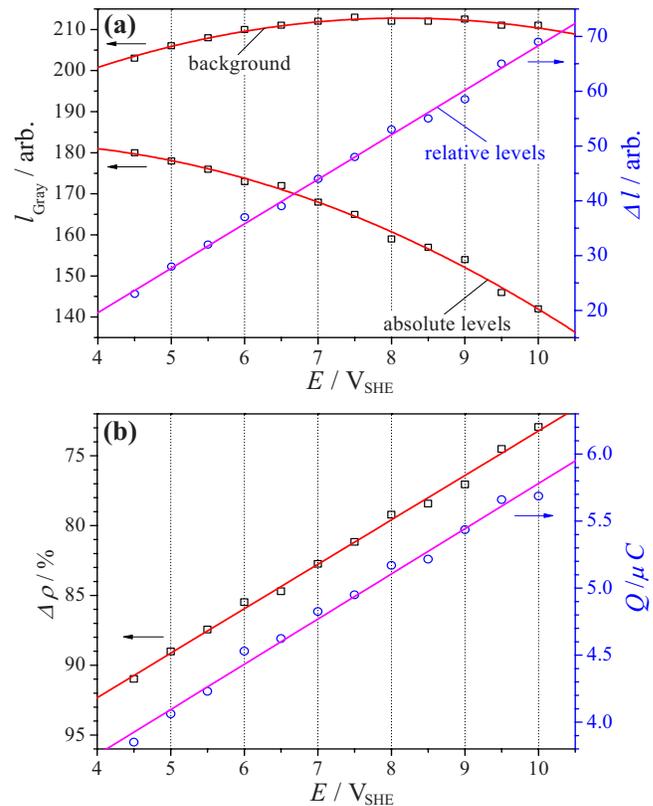


FIG. 3. (Color online) (a) The metallic background, absolute and relative grayscale levels of the oxide spots grown on Hf. (b) The relative reflectivity of the anodic oxide spots and the charge consumed for their growth at various potentials.

its usefulness for high throughput applications such as anodization of thin film combinatorial alloys.¹³

The curve presented in Fig. 2 does not indicate any dependence of the spots' area on the anodization potential. This is better observed in the inset of Fig. 2, where the optically measured areas of each of the Hf spots from a median line in the matrix are presented. Also in this case, a scatter of maximum $\pm 0.5 \text{ μm}$ can be observed in the mappings of the spots' radius along the anodization potential, confirming the previously measured deviation. The extremely low scattering of the optically measured areas of the anodic oxide spots grown on Hf at different potentials show that the confined droplet operation mode of the SDC acts toward inhibiting the natural tendency of droplet expansion, due to electrocapillarity. This represents a net advantage of this operation mode, as compared with the free droplet mode where an area uncertainty affects the interpretation of the electrochemical data such as current or charge measurements.

The oxide spots array presented in Fig. 1 shows a color gradient, the oxide color becoming darker at higher polarization potentials. In order to quantify this observation, a median line of oxide spots was closely investigated. After conversion of the matrix image into gray scale, a mapping of the gray levels on the surface was possible as a function of the applied potential. Figure 3(a) shows this mapping, the vertical scale being given as gray scale intensity levels (0 = black, 255 = white). The background levels of the metal imaged around each oxide spot showed a parabolic distribution

along the surface of the matrix, due to an illumination gradient during the optical imaging. The absolute levels measured inside each oxide spot decrease with the increase in the anodization potential. The difference between both curves is also represented in Fig. 3(a), with the vertical scale expressed as relative gray scale levels. The strictly linear dependence of the relative levels of the oxide spots on the anodization potentials can be directly related to the thickness of the oxides through an increased optical absorption for thicker oxides. This is better observed in part (b) of Fig. 3 where the relative reflectivities of the oxide spots (as reported to the background reflectivity of the metal) are presented together with the coulometric data obtained from the integration of each anodization curves. The correlation between both curves is extremely accurate, small oscillations of the charge being translated into oscillations of the reflectivity, as observed, e.g., at 6, 8, or 8.5 V. This investigation demonstrates that an optical microscope image can be precisely associated with the colorimetric features of nanometer-sized anodic oxide thicknesses.

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