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Nondestructive Characterization of Nanoporous Alumina Films Using Terahertz Scattering Imaging

Min Zhai,^{1,2} A. Locquet,^{1,2} Mi Jung,³ Deokha Woo,⁴
and D. S. Citrin^{1,2*}

1. Georgia Tech-CNRS UMI 2958, Georgia Tech Lorraine, 2 Rue Marconi, 57070 Metz, France
2. School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0250 USA
3. Konkuk University Global Campus, 268 Chungcheonbuk-do, 27478 Republic of Korea
4. Sensor System Research Center, Korea Institute of Science and Technology, Seoul, Republic of Korea

*Corresponding: david.citrin@ece.gatech.edu

Abstract

Ordered nanoporous (NP) alumina (Al_2O_3) films were grown on Al substrates through a two-step electrochemical anodization process. The morphology as well as the roughness are characterized by terahertz (THz) reflectometry and scattering imaging. In particular, we show that before the second anodization, irregular surface morphology of the NP Al_2O_3 films leads to significant THz scattering, whereas the far more homogeneous films following the second anodization show far less scattering. The regularity of the surface morphology is not readily ascertained using visible-light optical microscopy. The THz results are corroborated by field-emission scanning electron microscopy (SEM) and atomic-force microscopy (AFM), both of which are time consuming, not easy to operate, and can only provide local characterization of NP Al_2O_3 films on Al substrate. THz-based techniques thus allow for the rapid nondestructive characterization of the surface morphology of the entire NP Al_2O_3 films on the 10-100 μm length scale, important for a range of applications, while providing information over macroscopic scan areas, and obviate the need for sample preparation required by other common surface-morphology characterization techniques.

Keywords: Terahertz imaging, Nondestructive testing, Morphology, Nanoporous alumina film, Characterization.

Highlight:

- Terahertz scattering imaging has been applied to characterize the homogeneity of nanoporous alumina films on Al substrate after two-step anodization on a scale of 10–100 μm and above.
- Irregular surface morphology of nanoporous alumina films observed using terahertz scattering image is corroborated by field-emission scanning electron microscopy and atomic-force microscopy.
- The stratigraphy and thickness of nanoporous alumina films are obtained nondestructively based on terahertz images.
- Terahertz imaging may provide a reliable nondestructive and contactless modality to evaluate the quality of nanoporous coatings.

1. INTRODUCTION

Due to their optical transparency [1-3], thermal stability [1], biocompatibility [4], as well as the controllability of structural parameters [5], nanoporous (NP) alumina (Al_2O_3) films have attracted scientific and technological attention for nanotechnology and nanoengineering applications, such as drug delivery [4,6,7], electrochemical sensors [8,9], molecular transport [6,10,11], and solar-energy conversion [12]. Compared with bulk crystal Al_2O_3 , NP Al_2O_3 has higher hardness, corrosion resistance, and wear resistance [13].

Anodization is an electrochemical process used to form an oxide layer on the surface of the native metal [13]. Recently, the most commonly used anodization method to form highly ordered NP Al_2O_3 is a two-step process. Unlike the single anodization process, which may lead to nonuniform pores and interpore distances [14], a well-ordered NP array may result after the two-step process because the purpose of the first anodization process is the formation of pattern for the second anodization. The parameters of NP Al_2O_3 , such as diameter and depth, are controlled by the applied voltage, the composition and concentration of electrolyte, as well as the duration and temperature of the anodization [5,15].

To date, optical microscopy [16], scanning electron microscopy (SEM) [17-19], atomic force microscopy (AFM) [19,20], transmission electron microscopy (TEM) [19], infrared spectroscopy [21], and x-ray diffraction (XRD) [22] are the most common ways to characterize of NP Al_2O_3 . These techniques, however, have limitations for characterizing NP Al_2O_3 films. For example, limited magnification and the necessity of continuous focusing adjustment resulting from the height variation of NP Al_2O_3 films, make optical microscopy problematic in some ways for morphology characterization of NP Al_2O_3 film on Al substrate. Of course, by adjusting the depth of focus, this

problem can be to some extent mitigated, but at the cost of lower transverse resolution. Even though AFM can generate a three-dimensional image based on the surface morphology and height difference, it only provides surface, rather than depth, information. Moreover, because of the small scan image size and relatively long scan time, AFM fails to provide global and instant information with nano-scale lateral resolution. Infrared spectroscopy may be used for structural characterization of NP Al_2O_3 because of its ability to scan a relatively large area and provide fast inspection [23]. However, the approach presents several drawbacks, such as the potential of introducing damage into the NP Al_2O_3 film owing to overheating, as well as the limitations on the depth information provided. Since SEM can observe both the surface and cross-sections, it is the most appropriate method for the systematic study of the microstructure of electrically conductive materials. To have a better brightness variation and enhance the conductivity for improving difficult focusing problems and image distortions, sputtering a conductive layer on the Al_2O_3 film, in some cases, is necessary. This limits resolution to sputtered conductive grain size and the reuse of samples for other tests. Even though TEM may provide surface and subsurface information, laborious sample preparation, excessive power of electrons, and strict sample requirements limit its widespread use, especially in industries. XRD is mainly a laboratory tool due to the ionizing nature of x-rays. Finally, optical microscopy may not provide the resolution on a sufficiently fine scale. A nondestructive, noncontact, and nonionizing approach possessing micron scale resolution is thus highly desirable.

Terahertz (THz) electromagnetic waves, whose frequency range refers to 100 GHz to 10 THz range, can penetrate many electrically insulating materials that is opaque to visible and infrared light, and transparent to x-rays. THz radiation presents no known health risks to biological tissue at the power levels utilized [24]. To date, THz-based

techniques have been employed to characterize various materials, such as glass fibers [25,26], explosives [27,28], ancient paintings [29,30], automotive coatings [31], polymers [32,33], and steel products [34,35]. A key point is that THz-based techniques provide the combined capability of giving depth and morphological information over the 10-100 μm scale while enabling scanning over macroscopic areas, which are superior to both SEM and AFM approaches, that are limited to characterizing microscopic areas and require special training to instrumental operations as well as sample preparation.

In a previous work by the authors [16], THz birefringence of NP Al_2O_3 films fabricated by a two-step electrochemical anodization process, was characterized nondestructively by polarization-resolved THz spectroscopy. Moreover, the film thickness was calculated based on THz results and showed an excellent agreement with the value measured by cross sectional field-emission scanning electron microscopy. In Ref. [36], the authors employ THz quantum cascade lasers to conduct spatially resolved spectral analysis of powdered samples. Inhomogeneity in constituent concentrations is mapped out by the scattered signal. Though the approach is termed “diffuse reflection imaging,” no direct evidence of true diffusive nature is presented [37]. In the present study, THz reflective imaging and THz scattering imaging are employed to characterize the homogeneity of NP Al_2O_3 films, which is poor following the first anodization, but markedly regular following the second anodization. (We make no claim anent the diffusive nature of the scattering.) This scattered signal is likely to be due to a rough surface morphology as well as of inhomogeneous structure in the film itself, though our measurement does not provide a distinction between these two effects. Instead, we focus on the approach as a rapid and nondestructive diagnostic. These results are

corroborated by SEM and AFM. One area with rough surface morphology is observed in THz scattering images, which is validated by SEM measurement.

2. SAMPLE AND EXPERIMENT

The fabrication of self-ordered NP Al_2O_3 films on a grain-free aluminum foil (99.99%, 100 μm in thickness, Tokai Aluminum Foil Company) [38] is conducted by a typical electrochemical anodization process. The dimensions of the Al foil used in this research are 6.7 cm by 1.4 cm. Pretreatment to degrease the foil and to remove initial surface oxide are first performed. To minimize surface roughness of the starting Al foil, substrates are first prepared by electropolishing for 60 s with a bias voltage of 20 V in a 1:4 volume mixture solution of $\text{HClO}_4\text{:C}_2\text{H}_5\text{OH}$ at 3°C. Field emission scanning electron microscopy (FE-SEM, Hitachi S-4700) is used to characterize the surface morphology of the Al foil after the electropolishing process. The Al strips are removed and there are no obvious defects are found in FE-SEM images as shown in Fig. 2(a).

Subsequently, a two-step anodization process is carried out in a 0.3 M $\text{H}_2\text{C}_2\text{O}_4$ solution. The temperature of the reactive solution is set to 3°C. The duration of first anodization is 8 h at 40 V bias voltage, and the thickness of NP film is controlled by the anodization duration. A constant stirring process is maintained through the entire first anodization.

A $\sim 80\text{ }\mu\text{m}$ NP Al_2O_3 layer with a nonuniform layer on the top and a uniform layer on the bottom can be observed in cross-section FE-SEM, shown in Ref. [17]. Figure 2(b) displays the top view SEM image of the sample after the first anodization. It is relatively obvious that this formed NP Al_2O_3 film is irregular. Inhomogeneity may result from the generation of heat on the surface of electrolyte during the first anodization. Moreover, at the bottom of the NP Al_2O_3 layer, a compact dielectric oxide

barrier layer is formed after the first anodization. The structure of the barrier layer can be characterized by cross-section FE-SEM, shown in Fig. 3. The thickness of barrier layer ranges from 30 nm to 45 nm.

In order to improve the regularity of the NP nanoarray, the disordered NP Al_2O_3 film is removed using wet chemical etching with a 0.2 M CrO_3 and 0.4 M H_3PO_4 solution at $\sim 65^\circ\text{C}$ for ~ 6 h. A highly periodic nano-concave structure on the Al substrate is shown in Fig. 4. These pits serve as the template for the formation of the uniform NP Al_2O_3 film during the second anodization [39].

The second anodization is carried out using the same apparatus and under the same condition (temperature, concentration of solution, and bias voltage). Well-ordered hexagonal pore arrays are obtained as shown in Fig. 2(c), demonstrating that the irregular pore lattice after the first anodization does not adversely influence the formation of NP Al_2O_3 films during the second anodization. The pore diameter and interpore distance can be estimated based on top-view FE-SEM images. The interpore distance and pore diameter are 105 ± 5 nm and 33 ± 3 nm, respectively.

Pulsed THz reflective imaging and THz scattering imaging are employed in this study. A schematic diagram of the setup for reflective imaging, based on a TeraView TPS Spectra 3000, is shown in Fig. 1. In scattering imaging, the detector is placed off the specular direction. The generation of THz pulsed radiation is based on a photoconductive switch. Quasi-single-cycle THz pulses with bandwidth 60 GHz to 3 THz are generated in a biased GaAs antenna excited by an Er-doped fiber laser emitting sub-100-fs 780-nm pulses at 100 MHz repetition rate with average output power > 65 mW. Coherent detection of the reflected THz radiation is performed in a similar photoconductive-antenna circuit. By focusing the laser beam onto the photoconductive gap of a biased semiconductor emitter and using a similar receiver, a current

proportional to the THz electric field is measured. A delay line is used to change the difference in the optical delay between the incoming THz pulse and the probe laser pulse at the receiver. A bias is also applied across the emitter and receiver to generate a time-gated output signal.

The THz measurements were carried out in an air-conditioned laboratory at 22° C with humidity < 48%. Before the THz measurement, the reference pulse, *i.e.*, the THz pulse produced by the apparatus, was recorded by setting a bare metal plate (an excellent THz reflector) at the sample position. The sample was raster-scanned by a set of motorized stages moving in the *x*- and *y*- directions with step size 0.2 mm. The recorded reflected temporal signal at each pixel contains 4096 data points (corresponding sampling period T_s is 0.0116 ps) and is averaged over 10 shots per pixel to reduce the effect of noise.

3. RESULT & DISCUSSION

3.1 AFM CHARACTERIZATION

AFM (Dimension Edge, Bruker) is used next to characterize the surface morphology of the NP Al₂O₃ film. Figure 5(a) shows the typical AFM image of a NP Al₂O₃ film after the second anodization. High regularity of closed packed hexagonal cells with circular nanopores are seen. The pore diameter, the interpore distance as well as the regularity of the NP arrays can be calculated by analysis software through the line scan primary profiles of AFM shown in Fig. 5(b). The peaks and the valleys refer to walls and pores, respectively. The calculated interpore distance based on the interval between the peaks or valley regions is ~110 nm, within the range estimated using FE-SEM image presented in Fig. 2(c). Based on the primary surface morphology of NP Al₂O₃ film, the roughness profile can be obtained after applying a high-pass filter. The cutoff

wavelength of the high-pass filter applied here is 0.039 μm , because the waviness profile obtained through applying low-pass filter with the same cutoff wavelength to the primary surface profile, is comparable to the primary surface profile. Figure 5(c) is the roughness profile along the red line marked in Fig. 5(a). The presence of the nanoscale protrusions as well as the rugosity along the line lead to the distortion of the unevenness of the surface. The closer to these irregular areas, the rougher the surface would be. These nanoscale surface protrusions may result from the collapse of NP Al_2O_3 on the surface [19]. B-spline smoothing filter is utilized to extract the roughness information from the line-scan roughness profile. Unlike Gaussian smoothing filter, which has relatively obvious edge effect and large fluctuations [40], B-spline smoothing filter can guarantee a better performance of the roughness evaluation and has been adopted as a standard to evaluate the roughness [41]. Some stipulated evaluation parameters, such as the roughness average (R_a), the root mean square roughness (R_q), and the average maximum height of the profile (R_z), are estimated based on AFM results, to 1.644 nm, 2.275 nm, and 16.18 nm, respectively.

3.2 THz MEASUREMENTS

Because AFM fails to easily provide comprehensive information on the NP Al_2O_3 film and is quite sensitive to the surface fluctuations, THz measurements are performed next in a nondestructive fashion to characterize the samples after electropolishing, the first, and the second anodization, with the reflected THz signals in Fig. 2(d)-(f). The signal reflected from the electropolished Al substrate is shown in Fig. 2(d). It is essentially the same as the reference signal as the Al substrate is highly reflective to THz radiation.

The reflected signals in Figs. 2(e) and (f) are more complex. A typical signal reflected from the sample after the first anodization is shown in Fig. 2(e). Due to the inhomogeneous surface of the NP Al_2O_3 films in cross-sectional FE-SEM shown in Ref.

[17], reflections occur from features of various heights within the frequency-dependent spot size of the THz beam ($\sim 300 \mu\text{m}$ at 1 THz), resulting in a complex reflected pulse. Moreover, scattering (signal emitted in non-specular directions) is expected to be important due to the roughness, as we see below. We next turn to samples following the second anodization, for which the NP lattice is quite regular, and the surface morphology is flat. In this case, scattering is expected to be relatively weak. Four temporarily overlapped reflections of the incident reference signal (*i.e.*, echoes) are observed in Fig. 2(f). The first positive echo corresponds to the air/NP Al_2O_3 interface and the second positive echo corresponds to the NP $\text{Al}_2\text{O}_3/\text{Al}$ interface. The third and fourth echo are the multiple reflection signals as THz wave propagates in NP Al_2O_3 material, and the change of sign results from the phase shift as expected. The observation of the first two distinct echoes indicates that the two interfaces are smooth on the scale of the THz spot size and well defined. The time delay between these two echoes and a knowledge of the film's refractive indices enable us to measure the film thickness; this technique is known as time-of-flight tomography (TOFT).

As pointed out above, non-specular scattering is related to inhomogeneity. We explore scattering by varying the scattering (detector) angle ϕ while fixing the incidence (emitter) angle near normal incidence ($\sim 3^\circ$). Corresponding C-scans of the NP Al_2O_3 films after the first and second anodization process are shown in Figs. 6 and 7, where the contrast mechanism is the maximum amplitude of the scattered signal. The NP Al_2O_3 film lies only within a 1-cm diameter disk on the substrate, as presented in Fig. 8, while the remaining area is electropolished Al. Due to the beam divergence, to ensure a signal dominated by scattering, we need to choose $\phi > 10^\circ$. For $\phi > 10^\circ$, the strength of the scattered signal depends markedly on surface morphology. An inhomogeneous region between 0.7 cm and 1.1 cm in the x -, and 0.4 cm and 0.7 cm in

the y -direction after the first anodization step, and position 0.6 cm and 1.0 cm in the x - and 0.3 cm and 0.6 cm in the y -direction after the second anodization, is clearly seen in Figs. 6 and 7. As ϕ increases further, the overall signal level falls significantly, as seen in Fig. 9. The increasingly mottled appearance of the C-scans with increasing ϕ is due to the decrease in the signal-to-noise ratio (SNR) as ϕ increases. When ϕ reaches 35° , the C-scan is dominated by noise.

In order to investigate the surface morphology and nanopore arrangement of the disordered area, other additional measurements are applied subsequently. Because of the small view field of AFM, it is hard to provide a systematic investigation on the microstructure of NP Al_2O_3 film and significant contrast at one time. Therefore, top view FE-SEM measurements are employed, and the corresponding result is displayed in Fig. 10. Compared with the FE-SEM result for the well-ordered area presented in Fig. 2(c), there is a slight change of density, pore diameter, as well as inter-distance. These distortions contribute to the occurrence of non-specular scattering.

The origin of the disordered area is worthy of study. Based on previous works on NP Al_2O_3 surface morphology, several tentative reasons are presented as follows. (1) Transfer of substrate-related nanoscale defects into the NP Al_2O_3 disturbs the NP array order[42]. (2) Because some pits and bumps persist on the Al substrate even after electropolishing, seen in Fig. 2(a), those macro defects impact the formation of NP Al_2O_3 [43]. (3) Because the degree of NP order is largely determined by a certain value of anodizing potential, nonoptimal anodization parameters could lower the degree of pore order [44]. (4) Due to the long etching process (~ 6 h), etching during the first anodization process may be nonuniform, perhaps also connected to defects in the substrates as discussed above. Because of the complicated process of sample preparation, there is no consensus on the details of the roles of the above mechanisms.

Indeed, it is likely that the answer depends on various aspects of the materials and processes employed.

The stratigraphy of the well-ordered NP Al_2O_3 film can also be characterized based on THz B-scans along a cross-section using TOFT. Such a B-scan in Fig. 11 is along $y=0.4$ mm as shown in Fig. 7. The narrow bright band near optical delay ~ 10 ps corresponds to the top air/NP Al_2O_3 interface. In addition, the NP Al_2O_3 /Al interface as well as the multiple reflections at later delays can be identified clearly. It is noted that the reflection from the Al substrate occurs later in the regions with the NP Al_2O_3 film than from where it is absent, which is expected due to the refractive index $n > 1$ of the film. Based on the optical delay Δt between the 1st and 2nd echoes, and the refractive index n of Al_2O_3 within THz regime ignoring the air fill factors [45], which is ~ 3 , the Al_2O_3 film thickness is $c\Delta t/2n \sim 87$ μm with c the speed of light. This is in good agreement with destructive cross-sectional FE-SEM. More detailed discussions of thickness characterization of NP Al_2O_3 film by sparse deconvolution can be found in Ref. [17].

We also note that birefringence can be observed because of the anisotropy NP Al_2O_3 film [46]. The birefringence is relatively small and does not appreciably affect the film thickness determination. We refer the reader to Refs. [17,47] for details on birefringence discussion for NP Al_2O_3 film.

4. CONCLUSION

In this study, two anodization processes were used to form NP Al_2O_3 films on Al substrate. The NP diameter, depth, and lattice constant of NP Al_2O_3 films are measured by FE-SEM and AFM. A poorly ordered NP Al_2O_3 film is formed after the first anodization, exhibiting rough surface morphology. A smooth and ordered NP array is

formed after the second anodization. An area with rough surface morphology is identified for all samples from THz C-scan results even for NP Al₂O₃ films only after the first anodization process. The THz scattering results are corroborated by FE-SEM measurements. The thickness of NP Al₂O₃ films calculated based on THz results is in excellent agreement with destructive cross-sectional FE-SEM measurement. To conclude, THz reflective imaging and scattering imaging are useful tools to characterize the homogeneity NP Al₂O₃ films and other nanoscale materials with thickness in dozens of μm and above. The approach is noncontact, nonionizing, and nondestructive; it can serve as a complementary technique that covers a large area and can be used to identify regions that would warrant further examination with high-resolution techniques. Specifically, for the NP Al₂O₃ films, competing approaches, such as optical microscopy, AFM, and FE-SEM either lack the requisite resolution or may result in damage to the films.

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FIGURE CAPTIONS

Fig. 1. Schematic diagram of THz reflective imaging experiment.

Fig. 2. FE-SEM showing surface morphology after (a) electro-polishing, (b) first anodization, and (c) second anodization. Corresponding reflected THz signals are presented in (d)-(f).

Fig. 3. FE-SEM image of a barrier layer of NP Al_2O_3 film on Al substrate.

Fig. 4. Top-view FE-SEM for sample after etching following the first anodization process.

Fig. 5. (a) AFM image of NP Al_2O_3 film on Al substrate after the second anodization process; (b) the surface primary profile, and (c) roughness profile along the red line in Fig. 5(a).

Fig. 6. C-scans of sample after the first anodization process for various reflection angles with the polarization angle $\sim 0^\circ$ and incidence angle fixed (at $\sim 3^\circ$, *i.e.*, near normal incidence). The contrast mechanism applied here is the maximum amplitude of the scattered signal.

Fig. 7. C-scans of sample after the second anodization process for various reflection angles with the polarization angle $\sim 0^\circ$ and incidence angle fixed (at $\sim 3^\circ$, *i.e.*, near normal incidence). The contrast mechanism applied here is the maximum amplitude of the scattered signal. The horizontal line at $Y=0.4$ cm, marked “Cross-section”, is in reference to the B-scan in Fig. 11.

Fig. 8. Real image of the Al foil after the second anodization process. One 1-cm diameter disk region of NP Al_2O_3 is found on Al substrate.

Fig. 9. Maximum amplitude of reflected THz signal from sample after second anodization at different positions (x,y) as a function of scattering angle ϕ .

Fig. 10. FE-SEM image at disordered area.

Fig. 11. B-scan based on the raw data with the cross-section $Y = 0.4$ cm. Inset shows origin of echoes in reflected THz signal: 1st air/NP Al₂O₃, 2nd NP Al₂O₃ /Al, and 3rd and 4th multiple reflections.

FIGURES

(1)

(2)

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(10)

(11)