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Development of Quasi-Two-Dimensional Nb_2O_5 for Functional Electrodes of Advanced Electrochemical Systems

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Abstract**—**In recent times there has been a growing interest in the development of quasi-two-dimensional niobium pentoxide (Nb_2O_5) as a semiconductor for the potential electronic applications such as capacitors, filtration, dye-sensitised solar cells and gas sensing platforms. Therefore once the purpose is established, Nb_2O_5 can be prepared in a number of nano- and sub-micron-structural morphologies that include rods, wires, belts and tubes. In this study films of Nb_2O_5 were prepared on gold plated silicon substrate using spin-coating technique and subsequently by mechanical exfoliation. The reason this method was employed was to achieve layers of less than 15nm in thickness. The sintering temperature of the specimen was 800°C. The morphology and structural characteristics of the films were analyzed by Atomic Force Microscopy (AFM), Raman Spectroscopy, X-ray Photoelectron Spectroscopy (XPS).

Keywords**—**Mechanical exfoliation, niobium pentoxide, quazi-two-dimensional, semiconductor, sol-gel, spin-coating, two dimensional semiconductors.

I. Introduction

DEVELOPMENT of quasi-two-dimensional (Q2D) nano-sheets of MoO_3 and WO_3 by mechanical exfoliation has already opened a new direction in science and technology: Q2D nano-crystals [1]. In regard to the semiconductor oxides with the layered structure, it was shown that the unprecedented properties of these Q2D crystals may be tailored by reduction of the band gap and/or increase in the mobility with intercallation by H^+ or Li^+. The interest in nanostructured Nb_2O_5 has been continuously increasing due to its multifaceted structural and functional properties. Nanostructured Nb_2O_5 has a huge potential as an alternative to Ta_2O_5 and TiO_2 in such electronic applications as photovoltaics and gas sensing platforms [2]. With wide band gap, Nb_2O_5 is an *n*-type transitional metal semiconductor with an oxygen stoichiometry dependent bandgap ranging between 3.4 to 4.0 eV and high-*k* (between 33 to 40). Stoichiometric Nb_2O_5 is an insulator (conductivity, $\sigma = \sim 3x10^{-6}$ Scm^{-1}) and converts into semiconducting state ($\sigma = \sim 3x10^{-3}$ Scm^{-1}) with a decrease in oxygen stoichiometry ($Nb_2O_{4.8}$). Niobium pentoxide exists in many polymorphic forms. H-Nb_2O_5 (pseudohexagonal), O-Nb_2O_5 (orthorhombic), T-Nb_2O_5 (tetragonal) and M-Nb_2O_5 (monoclinic) are the most common crystallographic phases. Nb_2O_5 is very resistive to the thermal shocks and thermo-cycling, possesses high melting point and wide working temperature range. The dielectric constant value, quite superior to the Ta_2O_5 ($\varepsilon'_{Nb2O5} = 41$ vs $\varepsilon'_{Ta2O5} = 27$), and an almost half density (higher specific capacitance) are just some of the advantages for the passive electronic device components. Depending on applications, Nb_2O_5 can be synthesized in various nano- and sub-micron morphologies that include wires, rods, belts, particles and tubes.

Although there are a number of procedures for sintering nanostructured Nb_2O_5 with highly crystalline and stratified structures, the combination of sol-gel/exfoliation methods provides an important advantage for the development of Q2D nano-sheets since the mechanical exfoliation can be resulted in nano-crystals with the average thicknes of ~10-25 nm. New approaches to the development of Q2D nano-sheets are particularly attractive as they are capable of producing Q2D nano-crystals with advanced properties in comparison with many other conventional semiconductor oxide nanostructures. So far separated implementation of sol-gel and exfoliation techniques for development of Q2D nano-sheets has been predominantly concentrated on either dichalcogenides or MoO_3 and WO_3 semiconductor metal oxides [3]-[7]. These recent research reports have confirmed that when the semiconductor oxides can be nanostructured and further exfoliated down to Q2D nano-crystals, their bandgap then could be fine-tuned down to the reasonable level acceptable by the most of electronic and functional device applications.

In this work it is reported for the first time a possibility of the development Q2D Nb_2O_5 nano-sheets by combined sol-gel/exfoliation method. Moreover, a new approach is presented for mapping the electrical properties in Q2D nano-sheets with thickness below the 20 nanometers scale, with scanning probe microscopy measurements carried out in air and without damaging the sample by carefully controlling the tip–sample force. This is done by combining C-AFM and a new method that joints together the advantages of Intermittent Contact AFM (IC-AFM), *i.e.*, a spatial resolution below 20 nm and no sample damage, and C-AFM, *i.e.*, very high current sensitivity, and the possibility to record local *I–V* curves, allowing the analysis of charge transport properties. This new imaging mode, termed here time-resolved CSFS-AFM, also known as PeakForce TUNA™ is based on the simultaneous measurements of the topography and the current flowing between the tip and the sample from the real-time analysis of force–distance curves measured for a tip oscillating in the kHz

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regime, far below the resonance frequency of the cantilever. The images are reconstructed pixel by pixel in real-time by averaging force–distance data in a time scale similar to IC-AFM. This work also reveals for the first time the results derived by PeakForce TUNA™ on the developed Q2D Nb_2O_5 nano-sheets and their interfaces with the detailed information between the morphology of nano-sheets, their grain boundaries and the obtained properties of Q2D Nb_2O_5 nano-crystals providing direct comparison between the morphology and the electrical properties at the nanometre scale. Furthermore, it is investigated how the H^+ intercalation improves the electrical conductivity of the developed Q2D Nb_2O_5 nano-sheets. Finally, CSFS-AFM is applied to those nano-crystals to unravel the details of the current distribution at the grain boundaries interface.

II. Procedure

The prepared Q2D Nb_2O_5 nano-sheets were fabricated by three-step process: the initial deposition method was conducted via spin-coating, followed by annealing at 800°C and the last step in the sequence was that sintered Nb_2O_5 was subjected to the mechanical exfoliation to achieve super thin layers. After the samples were sintered and removed from the oven, they were conditioned at room temperature for seven days. All the reagents used in fabrication Nb_2O_5 nano-sheets were high-purity analytical grade and were applied as received. The main advantage of these Q2D nano-structures is that the electrochemical properties and morphological characteristics can be significantly improved by two factors: (1) controlling (reducing) the band gap by minimizing the thickness of nano-sheets and (2) increasing the mobility with intercalation by H^+ ions. The crystalline structures, surface morphologies and surface chemistry were examined by AFM, FTIR, Raman Spectroscopy and XPS.

Raman Spectroscopy was used to determine and identify the vibrational and rotational information regarding the chemical bonds and for this purpose μSense-L-532-B Laboratory Raman Analyser, US was employed. During the testing CCD detector was cooled down to -60°C. The spectra obtained were studied by RamanReader-M Software (Enwave Optronics Inc).

CSFS-AFM scanning probe technique combines the advantages of IC-AFM (in terms of spatial resolution) and C-AFM (in terms of current sensitivity). Similar to IC-AFM, the tip and the sample are intermittently brought into interaction while the sample is scanned. However, in CSFS-AFM, the feedback loop controls the force applied on the sample for each individual oscillation cycle. This direct force control protects the tip and the sample from scan-induced damage, but more importantly, it allows every tip–sample contact to be controlled and recorded to extract the current values while the tip–sample contact area is minimized. The two electrical modules are characterized by a very high sensitivity below 100 fA.

The oscillation frequency of the probe is set between 1 and 2 kHz, which is intermediate between IC-AFM (>50 kHz) and C-AFM (contact mode operation). This working frequency allows for the recording of the current values with an acceptable signal-to-noise ratio. When the tip is approaching the surface, the attractive forces (usually *van der Waals*, electrostatic, or capillary forces) pull the cantilever down toward the surface. When the forces overcome the cantilever stiffness, the tip is attracted by the surface, resulting in the dip in the approach curve (snap-in). Then, the force increases until the *Z* position of the modulation reaches its lowest poin. The force at this point is maintained constant by the system feedback during the interaction period. The tip then starts to withdraw and the force decreases until it reaches a minimum on the retract curve (pull-off), which coincides with the minimum contact force during the cycle. When the tip has come off the surface, no significant force acts on it. During scanning, a DC bias can be applied between the tip and the sample and the current passing through the sample when the contact is effective can be recorded.

The chemistry and crystal phase arrangement of the Nb_2O_5 nano-sheet was studied by X-ray photoelectron spectroscopy (XPS) using an AXIS Ultra DLD spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al Kα source at a power of 180 W (15 kV × 12 mA), a hemispherical analyser operating in the fixed analyser transmission mode and the standard aperture (analysis area: 0.3 mm × 0.7 mm). The total pressure in the main vacuum chamber during analysis was less than 10^{-8} mbar. Survey spectra were acquired at pass energy of 160 eV. The sample was analysed at an emission angle of 0° as measured from the surface normal. Assuming typical values for the electron attenuation length of relevant photoelectrons the XPS analysis depth (from which 95 % of the detected signal originates) ranges between 5 and 10 nm. Data processing was performed using CasaXPS processing software version 2.3.15 (Casa Software Ltd., Teignmouth, UK).

III. Results and Discussion

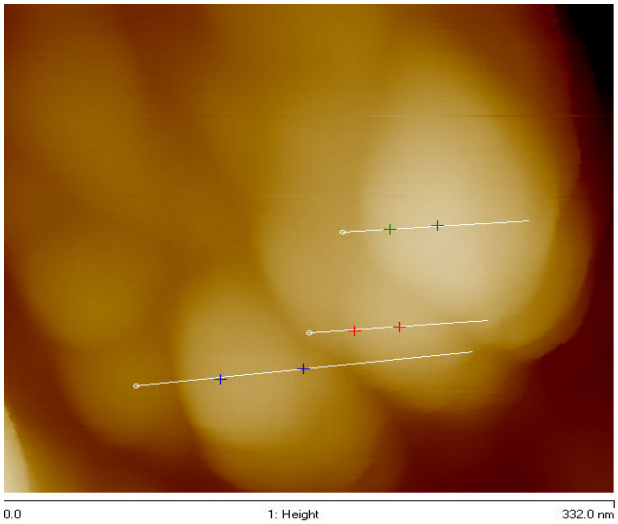

Fig. 1 AMF measurement of the developed structure of Q2D Nb_2O_5 nano-sheets deposited on quartz. Insert – height measurements of the individual Nb_2O_5 nano-sheets

Fig. 1 shows AFM measurements of the developed structure of quazi-2D Nb_2O_5 nano-sheets deposited on quartz with height data of individual nano-sheets. As has been clearly shown in this figure, the exfoliated nano-sheets of Nb_2O_5 still represent the layered structure consisting of 3 layers of Nb_2O_5 nano-flakes with the average measured thickness from 15 to 25 nm.

At the edges between the different regions an increased Fowler-Nordheim tunneling current represented the dark areas on the image (Fig. 2 B). This indicates local structural thinning of the oxide during the fabrication, which serves as an insulating area between adjacent active regions. Enhanced current flow is noticeable along the grain boundaries of Nb_2O_5 nano-sheet, whereas less current is observed on the individual nano-flakes. Significant contrast in colors for current/voltage measurements (Fig. 2 C) represents local variations in effective electrical thickness. It is evident that most often, areas with increased tunneling current seem to correspond with topographically elevated features. Analysis of adhesion image (Fig. 2 D) revealed that the developed Q2D nano-sheets had quite good adhesion to the quartz substrate (dark areas on nano-flakes, especially on those nano-flakes, which are directly contacted to the substrate).

Further investigation of the possibility of the progress of Q2D nano-sheets has shown that very small Nb_2O_5 nano-sheets with dimensions of about 40 x 60 nm and thickness as thin as ~5 nm may also be developed. Fig. 3 depicts 3D AFM image of those Nb_2O_5 nano-sheets on the quartz substrate with appropriate height measurements. In order to increase the mobility in the established Q2D Nb_2O_5 nanostructures, H^+ intercalation was completed by exposing these nano-sheets to the gas mixture (97% N_2 + 3% H_2) with controlled flow rate of 200 cm^3/min. The samples were mounted inside the chamber and were applied to the synthetic air for 30 min in order to remove any moisture and possible contaminants. Following this initial process, samples were subjected to the hydrogen-containing atmosphere for 5 min. After completion of the H^+ intercalation, CV measurements were performed by using PF TUNA™ on several points of interest: from the edge to the middle of the Q2D Nb_2O_5 sample. The summary results of these measurements are presented in Fig. 4.

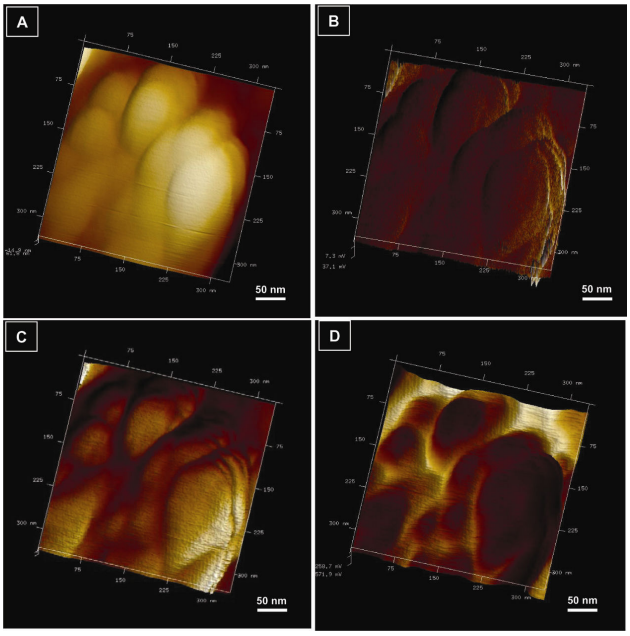

Fig. 2 Topography A, tunnelling B, current/voltage C and adhesion D images obtained simultaneously on Q2D Nb_2O_5 nano-sheets deposited on quartz substrate

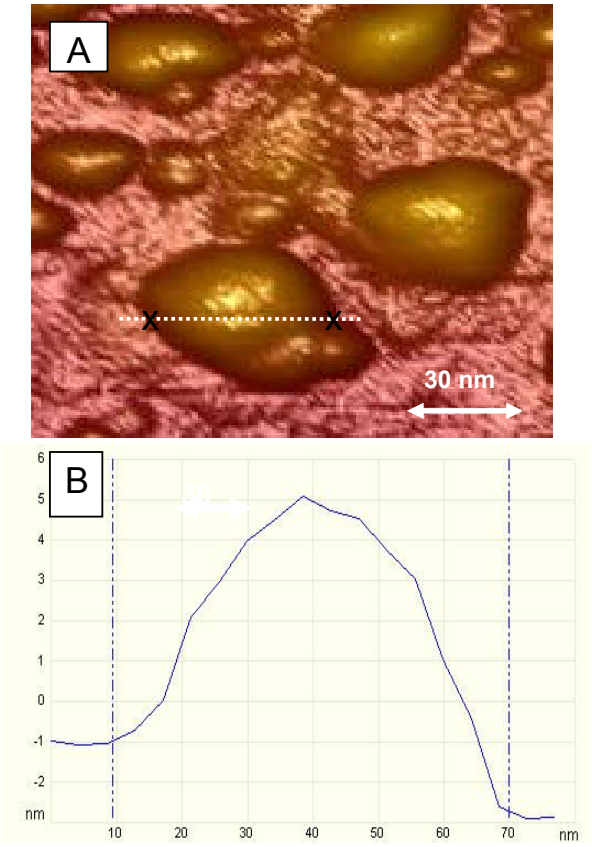

Fig. 3 3D AFM image of the developed Q2D Nb_2O_5 nano-sheets deposited on quarts A with height measurements B

It is apparent that the H^+ intercalation has increased conductivity of the Q2D Nb_2O_5 sample particularly on the edges (positions 1 and 3). However, in the middle of the sample the conductivity has not been increased. In summary, we have synthesized Q2D nano-sheets of Nb_2O_5 with average thickness of ~10-25nm by using combined sol-gel/exfoliation method. Additional electrochemical testing of the Nb_2O_5 samples intercalated by H^+ provided clear evidence of increase in conductivity of nano-sheets and ability of their use as material for various sensing platforms with definite advantage to the carries mobility.

Raman spectroscopy was employed to determine the vibration and rotation information in relation to chemical bonds and symmetry of molecules in both the micro-structured Nb_2O_5 film and Q2D Nb_2O_5 nano-sheets, with particular interest to the finger-print region of the spectra, presented in Fig. 5 for both samples. In general terms the graphs not only display significant peaks in the perturbation area of the spectrum (Fig. 5 B), but also demonstrate a number of substantial stretches with various magnitude in the region of 1400-2000 cm^{-1}. Two stretches observed at 482 cm^{-1} and 1526 cm^{-1} correspond to Si and Au, respectively, which are part of the substrate itself. Broad peak detected at 680 cm^{-1} confirms the presence Nb_2O_5 for both spectra. However, the intensity of peak for Q2D Nb_2O_5 nano-sheet was about three times higher than the intensity of the same peak for micro-structural Nb_2O_5. Distinctive peak observed at 1462 cm^{-1}, confirmed the strong existence of C-N bonds. The spike at 228 cm^{-1} indicated the presence of Nb-OH bond. There were no other peaks noted, suggesting that no impurities were present. Analysis of the FTIR spectra in Fig. 8 in addition to the Raman spectra in Fig. 3 confirms that Q2D Nb_2O_5 nano-sheets are much for sensitive than micro-structured Nb_2O_5 as component for the various plasmonic-based sensing platforms.

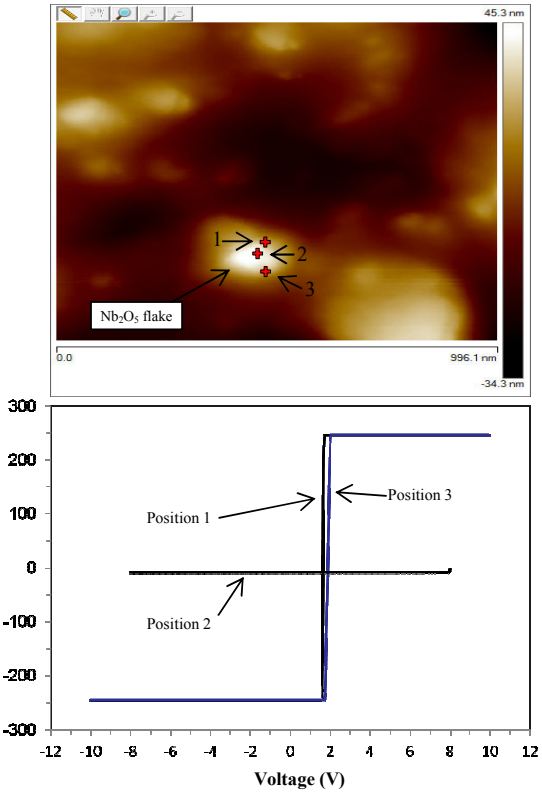

Fig. 4 PFTUNA^{TM} AFM images for Nb_2O_5 at three different positions on the flake with appropriate CV measurements for all three positions

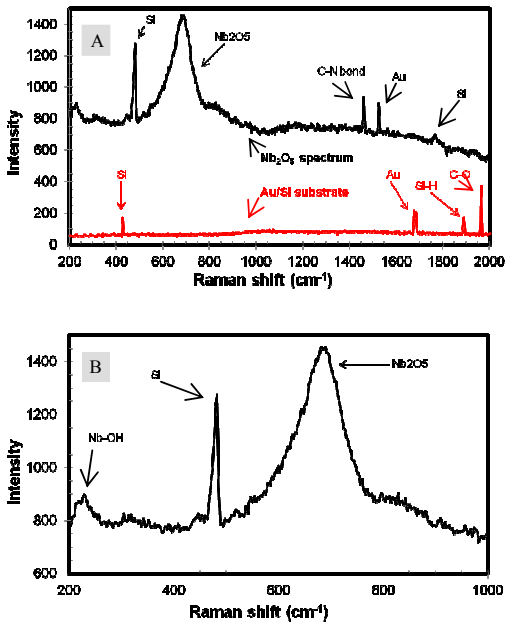

Fig. 5 Raman spectra for Nb_2O_5 and Au/Si substrate reference A; perturbation region within 200-1000 cm^{-1} B

In this study XPS analysis was used for examination of the surface chemistry of Nb_2O_5 nano-sheet by measuring its elemental composition and both chemical and electronic state of Nb and O within the sheet. XPS analysis of the Q2D Nb_2O_5 nano-sheets, presented in Fig. 6, shows the characteristic binding energy shape of the core level spectra for Nb 3d shell electrons and O 1s shell electrons. Complimented EDS measurement of the Nb_2O_5 nano-sheets (Fig. 7) clearly identifies niobium and oxygen as key components of the material. Due to the fact that the nano-sheets were not 100% dense, weak silica peaks were also observed. These signals are most probably because of the quartz substrate, which was used as a platform for all nano-sheets. As iridium was applied to coat the sample to improve the image quality, it is also present in the spectrum.

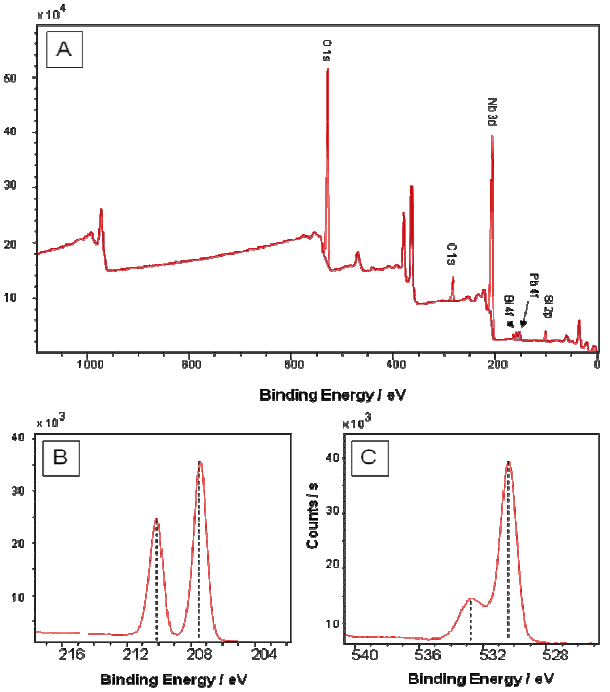

Fig. 6 XPS core level photoelectron peaks for Q2D Nb_2O_5 nano-sheets: (A) spectrum, (B) Nb 3d, (C) O 1s

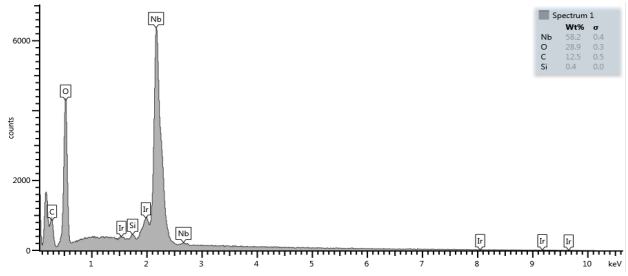

Fig. 7 EDS analysis of the developed Q2D Nb_2O_5 nanostructure

IV. Conclusion

In summary, Q2D Nb_2O_5 nano-sheets have been developed with the average thickness of ~15-25 nm using combination of the sol-gel/exfoliation techniques. Controllable increased conductivity of these Nb_2O_5 nano-sheets can be achieved through the use of the appropriate H^+ intercalation process. It was confirmed that the Raman finger-prints from the Q2D Nb_2O_5 nano-sheets were significantly amplified compared to the micro-structured Nb_2O_5, particularly in the low-frequency region. Additional electrochemical testing of the Nb_2O_5 samples intercalated by H^+ provided clear evidence of the increase in conductivity of the developed nano-sheets and the ability of their use as a potential nano-material for various sensing platforms with definite advantage to the carrier mobility. Therefore, the presented Q2D Nb_2O_5 nanostructures offer exciting opportunities in applications such as dye-sensitized solar cells, capacitors, photovoltaics, filtration and sensing platforms.

The nanoscale morphology and the electrical properties of the developed Nb_2O_5 nano-sheets have also been studied in this research. The morphological analysis confirmed the tendency of Q2D Nb_2O_5 nano-sheets to form multi-layers with common orientation. The combination of C-AFM and CSFS-AFM provided valuable information on the electrical properties of nano-material, showing that the current is governed by the spreading resistance at the tip-sample contact, resulting in high-resolution current contrast (below 10 nm) related to the local electrical properties of the investigated nano-materials. It was also possible to analyze simultaneously several characteristics not only the nano-material itself, but also its grain boundaries. The use of CSFS-AFM thus opens up the prospect of effective investigation of the electrical properties of nano-materials connected to their appropriate morphology at nanometer scale, i.e., where the phenomena actually occur, which is not possible to do by using the conventional AFM analysis.

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