Electronic Supplementary Information

for

Solution-processed ultra-low-\textit{k} thin films comprising single-walled aluminosilicate nanotubes

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EXPERIMENTS

Synthesis of AlSiNTs

Aluminum-tri-sec-butoxide (Sigma-Aldrich, 97%) was mixed with tetraethyl orthosilicate (Sigma-Aldrich, 98%) under argon. The mixture was immediately added to a 0.038 M perchloric acid solution. The molar ratio of Si:Al:HClO₄ in the mixture was 1:2:1. This aqueous solution was stirred at room temperature for a period of 24 h. Following this aging stage, the solution was diluted by a factor of 3.8 using deionized water and then heated to 95 °C. When the temperature reached 95 °C, the solution turned from turbid to transparent within 1 h. The solution was then heated to 95 °C under pressure of one atmosphere for four days. The as-synthesized AlSiNT aqueous solution comprised approximately 0.1 wt% of AlSiNTs. The solution was then concentrated under reduced pressure using a rotary evaporator to reduce the volume by a factor of 10, wherein the final concentration of AlSiNTs in the solution was about 1.0 wt%. The resulting solution was dialyzed against deionized water using a dialysis membrane of 12 kDa over a period of 3 days. The resulting AlSiNT aqueous solution was used for the fabrication of AlSiNT thin films, as outlined in the following section.

Fabrication of AlSiNT Thin Films

We investigated two cast solutions in this study. The first solution comprised as-made 1.0 wt% AlSiNT solution and the other was the same AlSiNT solution with an addition of poly(vinyl alcohol) (PVA) as a stabilizer. The cast solution with PVA was produced by combining 0.01 g of PVA (Sigma-Aldrich, 98-99% hydrolyzed, MW 146,000-186,000) with 10 g of 1.0 wt% AlSiNT solution. The mixture was stirred at 80 °C for 2 h until the PVA was entirely dissolved. The solution was cooled down to room temperature prior to thin film casting. The substrate was
prepared for the AlSiNT thin film casting by depositing an 80 nm layer of chromium on a 1 inch × 1.5 inch Corning glass using an electron beam evaporator (Kao-Duen Tech). Regular glass, instead of Corning glass, would yield poor thin film morphology. The AlSiNT thin film was cast on the substrate using a spin coater. The substrate was then covered by the cast solution and spun at 400 rpm for 30 s. The sample remained spinning at 400 rpm for 2 min, during which an air blower was used to gently circulate air at room-temperature in order to dry the cast solution on the substrate, resulting in the formation of a thin film. The coating procedure was repeated two more times on the same substrate in order to thicken the thin film. A thin film of pure PVA was prepared as a control sample. The cast solution for the pure PVA film comprised 5 wt% PVA in water. The coating procedure was the same with the preparation of AlSiNT thin films, except the spin coating was conducted for only one time.

Morphological Characterization

Optical microscopy (OM): an optical microscope (Olympus AH-3) equipped with a digital camera was employed for the imaging of the AlSiNT thin films.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS): a JEOL JSM-7600F field emission scanning electron microscope equipped with energy dispersive spectrometer (Oxford Instruments INCA X-sight LN2 EDS) operating at an accelerated voltage of 10 kV was used to investigate the micromorphology of the AlSiNT thin films.

Cryogenic transmission electron microscopy (cryo-TEM): AlSiNT solution of 0.1 wt% was vitrified to a thickness of approximately 200 nm on a QUANTIFOIL® TEM grid and kept below -178 °C during observation. A Philips/FEI Tecnai G2 120 kV LaB6 TEM with cryogenic capability was used for the imaging of quasi-solution-state samples.
**Nitrogen Physisorption**

Nitrogen physisorption measurements were conducted using a Micromeritics 3Flex Surface Characterization Analyzer. Isotherms were obtained using a 3Flex surface characterization analyzer at 77 K. The powder samples were degassed at 150 °C in a vacuum chamber at 10⁻³ Torr for 12 h prior to measurements. The powder samples were produced by drying the cast solutions in a convective oven at 105 °C.

**FT-IR spectroscopy**

FT-IR spectra of the powder and the thin film samples were acquired using a JASCO FT/IR-6700 spectrometer with a diffuse reflectance accessory, using KBr as a background. The AlSiNT thin film was scraped from the substrate for measurement. Each FT-IR spectrum was obtained from 100 scans at a resolution of 4 cm⁻¹.

**Grazing-incidence wide-angle X-ray scattering (GIWAXS)**

GIWAXS patterns of AlSiNT films cast on a glass substrate were obtained using a Rigaku Nano-Viewer with CuKα radiation of 40 kV and 30 mA with a two-dimensional detector (Rigaku, 100K PILATUS). Scattering vector, \( q \), was calibrated using a standard sample composed of silver behenate. The GIWAXS patterns were obtained in a grazing-incidence mode (GIWAXS) with an incident angle of 0.2° using a sample-to-detector distance of 98 mm and an exposure duration of 4 h. The resulting patterns were processed using Rigaku 2DP software.

**Grazing-incidence small-angle X-ray scattering (GISAXS)**
GISAXS images of the AlSiNT films cast on a silicon wafer substrate were obtained as a control sample. This GISAXS pattern was obtained using the facilities at beamline 23A station at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. We employed incidence X-ray energy of 15 keV (0.8267 Å) and a sample-to-detector distance of 2623 mm. The incidence angle of each X-ray beam was 0.2°. Scattering patterns were recorded using a Flat Panel CMOS detector with a 10-second exposure. The acquired 2D scattering patterns were processed using proprietary LabVIEW-based software developed by the station. The Reflex module in the BIOVIA Accelrys Materials Studio 7.0 was used for the simulation of X-ray scattering patterns. Details of the simulations have been reported previously.¹⁻³

Nanoindentation

Nanoindentation tests were conducted at room temperature using a Hysitron TI 950 TriboIndenter. We employed a 13 μN/second loading/unloading rate and 5-second dwell-time in the testing of all samples. The indenter was equipped with a Berkovich (with half angle 65.3˚) pyramidal diamond tip. The Young’s modulus and hardness of the thin-film samples were deduced from the raw data of the nanoindentation tests.

Dielectric Properties

An array of circular chromium patterns with a diameter of 0.5 mm and thickness of 80 nm was deposited on the top of the AlSiNT thin films, which were cast on chromium-coated glass via electron beam evaporation. A chromium pattern spot on the AlSiNT thin films with the chromium layer underneath it was electrically contacted to measure the capacitance of the AlSiNT thin films. These measurements were performed using a semiconductor characterization
system (Keithley 4200-SCS). In a typical measurement, 10 pattern spots were probed and the results were averaged. The relative permittivity ($\varepsilon_r$), also known as dielectric constant $k$, of the thin films was calculated using the relation $\varepsilon_r = C \cdot d / (\varepsilon_0 \cdot A)$, where $C$ is the measured capacitance, $d$ is the film thickness (determined from cross-sectional SEM images), $A$ is the area of the pattern spot, and $\varepsilon_0$ is the vacuum permittivity ($8.854 \times 10^{-12}$ F·m$^{-1}$).

Dehydrated AlSiNT thin films were prepared using the following procedure for the measurement of capacitance. Thin film samples were placed in a sealed vessel and heated to 150 °C under a reduced pressure of 0.01 mmHg for 12 h. The capacitance measurements for dehydrated AlSiNT thin films were conducted under purged nitrogen to prevent exposing the samples to moisture.

Rehydration of the AlSiNT thin films was achieved by placing the dehydrated samples in a sealed container under 80% relative humidity. The rehydration duration ($t_h$) was set to 10, 30, 60, or 120 min, respectively. Following rehydration, capacitance measurements were carried out.

Refractive Index

The refractive index of the AlSiNT films was obtained using a Raditech SE-3 ellipsometer at a fixed incidence angle of 70.0° in the spectral range of 400–1000 nm. Modeling, fitting, and regression of the ellipsometric data were performed using the software supplied by the manufacturer of the instrument.
Fig. S1 FT-IR patterns of AlSiNT thin film and pure powders of AlSiNTs and PVA.
**Fig. S2** Top-viewed (a) photograph and (b) optical microscopic image of AISiNT thin film prepared with poly(ethylene imine) (PEI) (MW = 800) as the stabilizer and Cr-coated glass as the substrate. Top-viewed (c) photograph and (d) optical microscopic image of AISiNT thin film prepared with PVA as the stabilizer and Si wafer as the substrate.
Fig. S3 Larger-$q$-range GIWAXS pattern of AlSiNT thin film spin cast from AlSiNT solution with added PVA.
Fig. S4 GISAXS pattern of AlSiNT film drop cast on a silicon wafer.
Fig. S5 Nitrogen physisorption isotherms of AlSiNTs and PVA in powder form.
SUPPLEMENTARY REFERENCES

