# Supplemental information for
## Cryogenic plasmas for controlled processing of nanoporous materials

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## Experimental

Treatment of the nanoporous film with cryoplasma:

Nanoporous films about 0.9 μm thick on Si were exposed to an $O_2$/Ar 10:100 plasma mixture at high pressure (100Torr). A parallel plate dielectric-barrier-discharge configuration[1,2] was used in a chamber that can be cooled down to a few tens of kelvins using liquid $N_2$ (LN) refrigeration to generate a cryogenic plasma environment. The control of the LN flow, and a calibrated heater system places underneath the LN tank under the chamber help to control the chamber and thus the plasma temperature. The gas temperature is measured with a Teflon-covered miniature thermocouple with an accuracy of ±2.2 K, placed at the gas inlet. More details on the experimental cryoplasma chamber can be found in Noma et al[3]. Typical electron densities for Dielectric Barrier Discharge are in the $10^9$-$10^{11}$ $e^-/cm^3$ range[4]. The plasma is monitored by naked eye through a quartz window, as well as with an oscilloscope measuring the applied plasma voltage and current, and by means of Optical Emission Spectroscopy (OES).

Characterization techniques:

After sealing the porous films with a 25nm sputtered Fe layer, conventional TEM cross section samples were prepared using a liquid nitrogen stage equipped Ar ion-mill with low energy guns. The TEM was done at 200kV using a JEOL 2010F equipped with an Enfina1000 EELS spectrometer and a liquid nitrogen cold stage operated at -120ºC. EELS line profiles were produced plotting relative concentration of elements as a function of position in the films using 50.4eV integration windows of background subtracted spectra and EELS cross sections calculated by ELP within the DigitalMicrograph software.

Specular x-ray reflectivity measurements were used to determine samples density, thickness and roughness. These measurements were performed using a diffractometer (X'Pert Pro MRD, Panalytical) with ceramic x-ray tube (wavelength=0.154 nm) and high resolution horizontal goniometer (reproducibility +/- 0.0001 degree). The reflected X-ray intensity is measured as a function of detector angle scaled to unit incident intensity. Subsequently, from such curves electron density and thus material density profiles is fitted with a curve calculated by dividing the total layer into an appropriate number of homogeneous layers. Density, thickness, roughness and X-ray absorption coefficients of each layer are fitting parameters[5].

## References supplemental information

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[2] M. A. Liebermann and A. J. Lichtenberg, in *Principles of Plasma Discharges and Materials Processing* (Wiley, New-York, 2005), p. 6-40.
[3] Y. Noma, J. H. Choi, S. Stauss, T. Tomai, and K. Terashima, Appl. Phys. Express **1,** 046001/1-046001/3 (2008).
[4] X. M. Zhu and M. G. Kong, J. Appl. Phys. **97,** 083301/1-083301/6 (2005).
[5] Y. Travaly, J. Schuhmacher, A. M. Hoyas, M. Van Hove, K. Maex, T. Abell, V. Sutcliffe, and A. M. Jonas, J. Appl. Phys. **97,** 084316/1-084316/9 (2005).

## XRR measurements and analysis

Figure S1 compares the measured XRR curves for the untreated (pristine) porous film and the films exposed to $Ar/O_2$ plasma at room and cryogenic temperatures. The reflected X-ray intensity is measured as a function of detector angle scaled to unit incident intensity.

The curves show that the pristine film has been modified upon plasma exposure and that the exposed films are densified, as shown by the shift of the critical XRR angle towards higher incident angles. Subsequently, from such curves electron density and thus material density profiles can be fitted with a simulated curve which is calculated by dividing the total layer into an appropriate number of homogeneous layers. The fitting of the experimental data for three layers of different density, thickness and roughness is obtained using a genetic algorithm (X'Pert Reflectivity software). Fitting using the Genetic algorithm is described, for example by: A. D. Dane, A. Veldhuis, D.K.G. de Boer, A.J.G. Leenaers and L.M.C. Buydens. Physica B **Vol 253** (1998) p254. Density, thickness, roughness and X-ray absorption coefficients of each layer are fitting parameters. Note that

the use of a large number of layers only makes sense if the difference in electron density between the layers is sufficiently large.

It is understood that the densities obtained here from the fitting represent an “average value” when the film has been gradually modified through its thickness. Nevertheless, the XRR analysis provide a good description of the depth modification of the films, and a very good agreement is found between the experimental curves (shown) and the fitting curves generated by a 3-layer model.

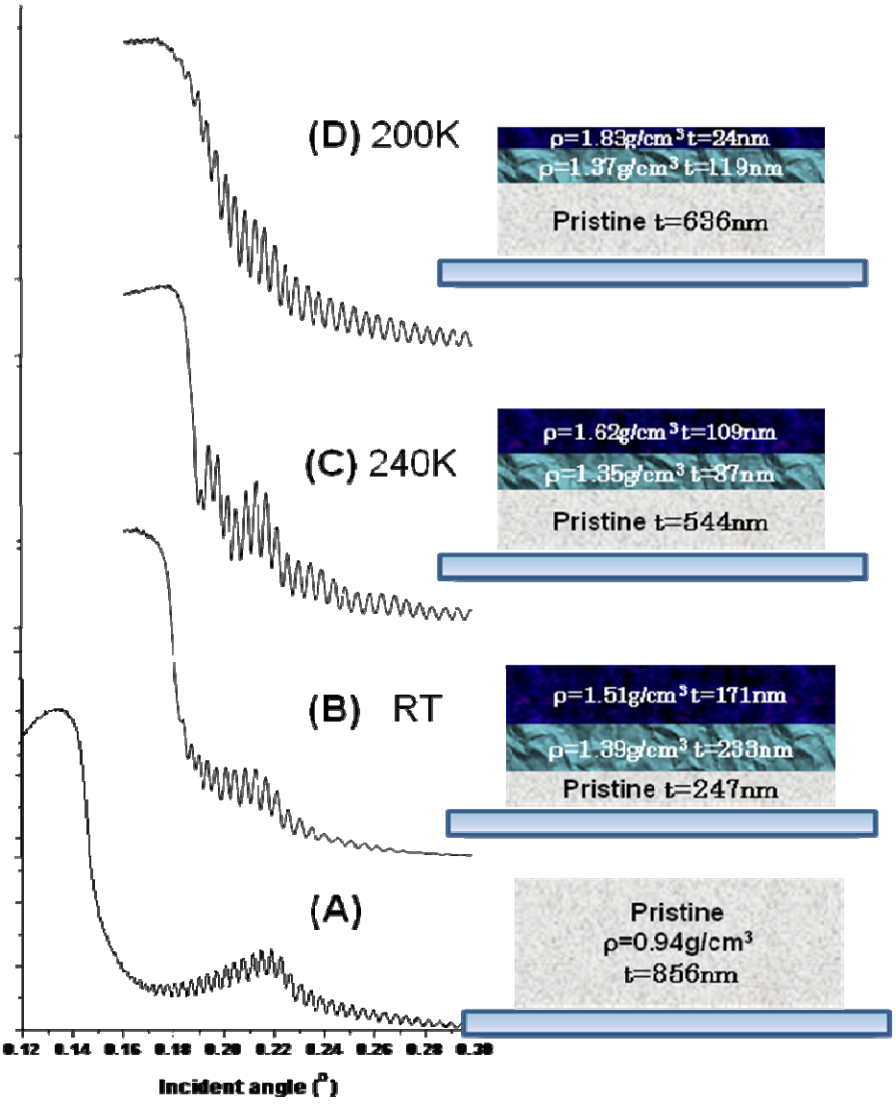


**Figure S1** XRR data and schematics of the film shrinkage (not-to-scale) and densities before (A) and after plasma exposure at room temperature (RT, 296K) (B), 240K (C) and 200K (D).