Learning about cupric oxide thin films and nanowires from the Raman lineshape

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Te Whare Wānanga o te Ūpoko o te Ika a Māui

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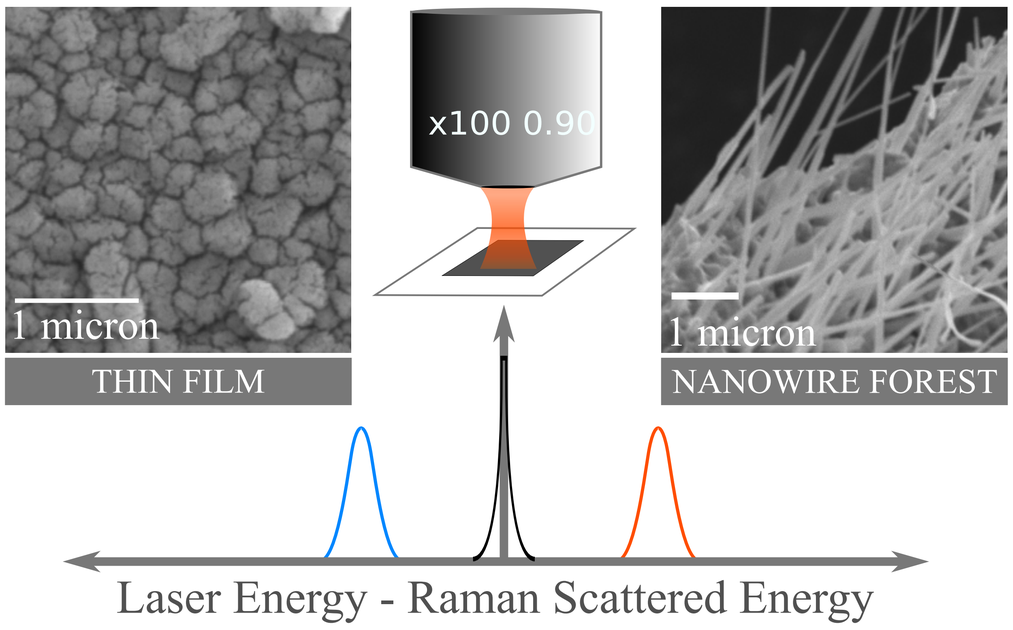
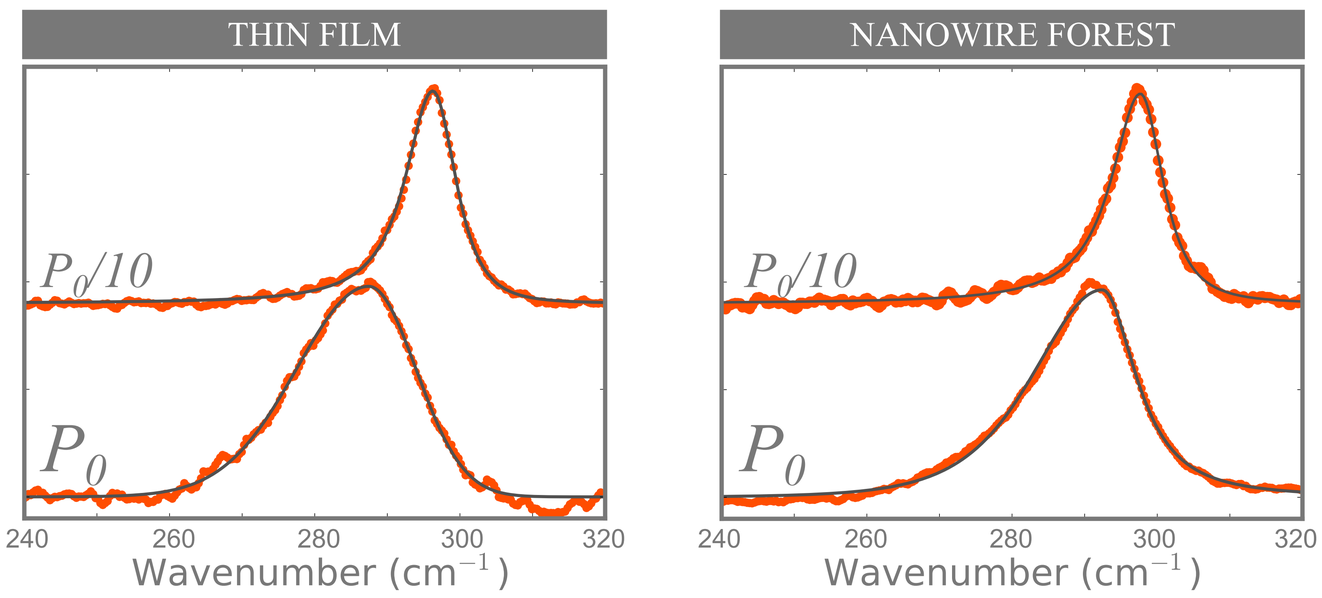
Raman spectroscopy reveals a subset of vibrational modes for a given molecule or crystal through the loss (or gain) of energy from a photon to (from) a vibrational mode. The Raman shift shows the energies of these vibrational modes in wavenumbers (cm^{-1}). The position and number of these modes usually correspond to a specific material. In the case of the material we have studied, cupric oxide (CuO), the three peaks at 298 cm^{-1}, 345 cm^{-1} and 630 cm^{-1} readily identify it from its close brother, cuprous oxide (Cu_2O). Aside from its use for detecting materials, Raman spectroscopy can also be used to probe local properties such as the temperature, chemical environment, structural variations and stress. These properties are typically understood through a detailed analysis of the lineshape (peak width and position) across the sample. In this study, we demonstrate the effects of laser heating on the Raman lineshape of two morphologies of CuO.



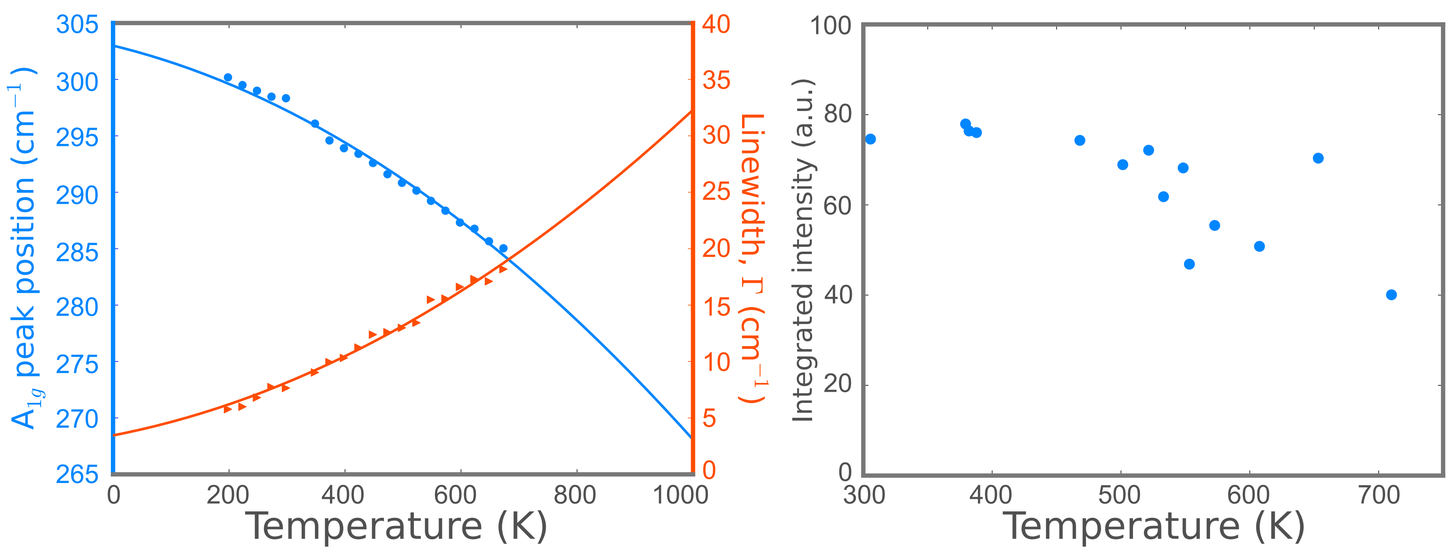


Power dependence

The two morphologies that we have studied are a nanocrystalline thin film (far left) and a nanowire forest (adjacent left). We only analyse the lineshape of the peak at 298 cm^{-1} since it is far stronger than the remaining peaks. From the spectra taken at different laser power, we find that the broadening and shift recover to the same values at low powers. However, the lineshape is quite different for the two samples at full power. The full power spectrum is symmetrically broadened for the thin film but is decidedly asymmetric for the nanowire forest. This is likely a temperature effect.

Temperature dependence

The local temperature of the sample can be easily affected by the tightly focused laser beam. The results of a temperature dependence study on the thin film (at low power) are given on the right. First, we find that the behaviour of the peak position and linewidth are described best by just accounting for phonon decay. Second, we note an interesting decrease of the integrated intensity (or number of Raman scattered photons) with temperature. This decreasing signal with temperature could be attributed to increasing absorbance with temperature.



Lineshape asymmetry from temperature

The symmetric broadening and red-shifting of the Raman mode in the thin film with increasing laser power can now be easily converted into a temperature. This equivalence between heating by a small laser spot (diameter ~ 2 microns) with a gaussian intensity distribution and global heating of the entire sample is likely due to spatial homogenisation of temperature by conduction. In the case of the nanowire forest we have a slightly different picture. The nanowires are thermally isolated from each other and temperature homogenisation by conduction is not possible.

The figure on the left shows a qualitative picture of the nanowire forest heating to different temperatures depending on the incident intensity. It could be argued that the signal from the regions with largest intensity (and thus temperature) will dominate the observed Raman spectrum. However, we learned in the previous section that the Raman signal decreases with increasing temperature. Hence, the Raman spectrum can be decomposed into contributions from an almost continuous distribution of temperatures from across the sample (middle and right). This simple description is rather powerful as it allows us to probe further into the values of the observed maximum and minimum temperatures for a given laser power. These values can then be used to infer processes of heat dissipation within the sample.