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Quantify doping efficiency at the nanoscale using monochromated STEM-EELS

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Doping is an important process for tailoring the electrical and optical properties of semiconductors for specific applications. Doping efficiency, defined by the ratio between charge carrier density and dopant density, is often very limited and varies significantly with the chemistry of the materials[1]. Despite its importance, quantifying doping efficiency usually requires multiple techniques and is only done at macroscopic scales.

Identifying individual dopant atoms has been made possible by Z-contrast imaging with aberration-corrected scanning transmission electron microscope (STEM)[2]. Electron energy loss spectroscopy (EELS) can provide additional information on the location of dopants[3], and is especially useful when a dopant's atomic number is close to that of the host lattice. Recently, monochromated EELS in STEM has emerged as a new way to directly probe the plasmons of free carriers in doped materials with spatial and meV energy resolution[4].

In this talk, we present doping efficiency quantified by monochromated EELS in a Nion UltraSTEM 100. Carrier and dopant densities have been obtained from low-loss (< 1 eV) and core-loss EELS signals, respectively (Figure 1). Unlike the 5-50eV valence electron energy loss, both ions and free charge carriers in a solid can participate the collective excitations in the infrared spectral range. With increasing doping, properties of the free carriers dominate the low-loss dielectric response of the material. We find the doping efficiency is of order 50% for La-doped $BaSnO_3$ (BLSO) bulk single crystals grown by the float zone method. Whereas for a Sn-doped In_2O_3 (ITO) film deposited by sputtering, the doping efficiency is no more than 30% (Figure 2). Free carrier plasmons in a freestanding ITO film will first be presented to show how we simulate the low-loss dielectric response, e.g., the surface and bulk contribution to the total energy loss, as well as the spatial resolution of the technique[4]. We will then discuss results on ITO and BLSO nanostructures to illustrate how the nanoscale shape and size influence the resonance energy and line width in low-loss EELS.

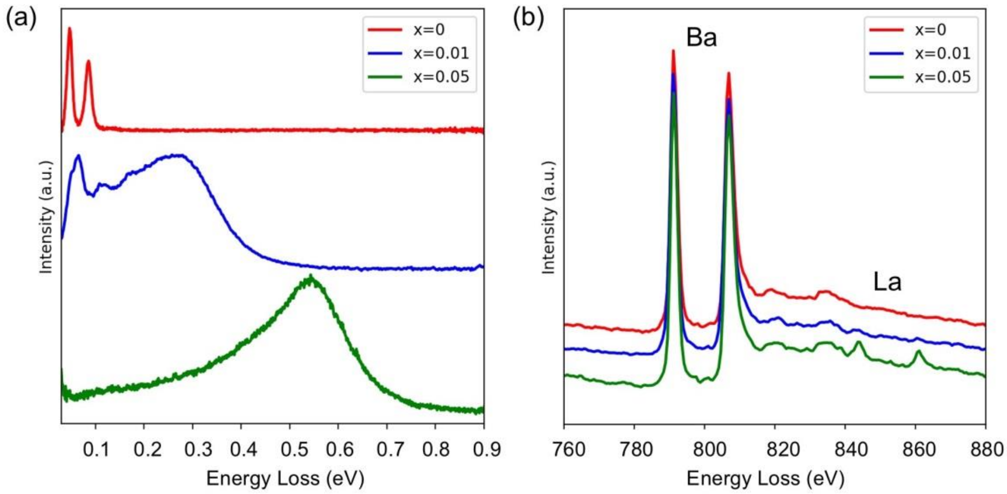

Figure 1. Figure 1. (a) Low-loss EELS acquired in the aloof geometry near Ba1-xLaxSnO3 crystals with large, cleaved surfaces. (b) Core-loss EELS showing Ba and La M4,5 edges, signals associated with La increase in intensity with doping.

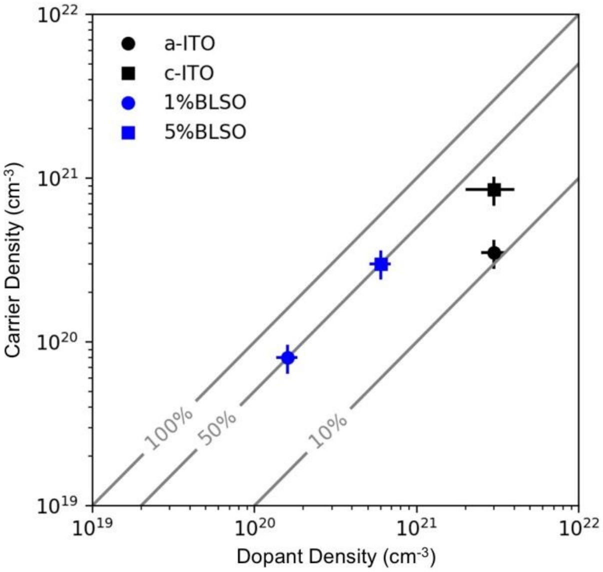

Figure 2. Figure 2. Dependence of carrier density on dopant density for ITO and BLSO. a-ITO and c-ITO indicate amorphous and polycrystalline ITO film, respectively.

References
1. G. V. Naik, V. M. Shalaev and A. Boltasseva, Adv Mater **25** (24), 3264-3294 (2013).
2. P. M. Voyles, D. A. Muller, J. L. Grazul, P. H. Citrin and H. J. L. Gossmann, Nature **416** (6883), 826-829 (2002).
3. M. Varela, S. D. Findlay, A. R. Lupini, H. M. Christen, A. Y. Borisevich, N. Dellby, O. L. Krivanek, P. D. Nellist, M. P. Oxley, L. J. Allen and S. J. Pennycook, Physical Review Letters **92** (9), 095502 (2004).
4. H. Yang, E. L. Garfunkel and P. E. Batson, Phys. Rev. B **102** (20), 205427 (2020).