Secondary Electron ARPES for Empty-State Band Mapping.

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Here it is proposed a new technique to study the empty-states of solid state materials. For many key applications in electronics, optics, thermionics it is crucial to map the empty-states to derive information such as bandgap, carrier effective mass in conduction band minimum (CBM), intra bandgap states and band alignments.

To characterize materials conventionally, photoemission related techniques, such as x-ray photoemission spectroscopy or valence band spectroscopy, focus on filled states below the Fermi level. We found an easy method to study also the empty-states that are above the Fermi level, therefore providing information on the conduction band. This approach is based on the study of secondary electron emission by angle resolved photoemission, Fig. 1, and it is feasible without access to synchrotron radiation facilities or complex equipment; indeed, we present results obtained using a laboratory-based photoemission electron microscope setup equipped with conventional VUV light sources.

Diamond represents an exemplary material where this new technique can be applied. When hydrogen terminated, diamond exhibits negative electron affinity (NEA), with the work function level that falls into the band gap and allows an accumulation of thermalized, hot electrons at the CBM [1,2]. Observing the angle-resolved secondary electron emission of two diamond crystals, with (100) and (111) orientations, it was possible to derive the photoemission rules of the secondary electrons. Exploiting these findings, we calculated the bandgap and carrier effective mass at the CBM. The effectiveness of this method was also verified using a no-NEA material, such as a copper crystal, confirming its general applicability.

Having an easy access to information of the materials empty-states is the springboard for a highly accurate electronic band engineering and represent a powerful tool to tailor advance materials optics, catalysis and electronics.

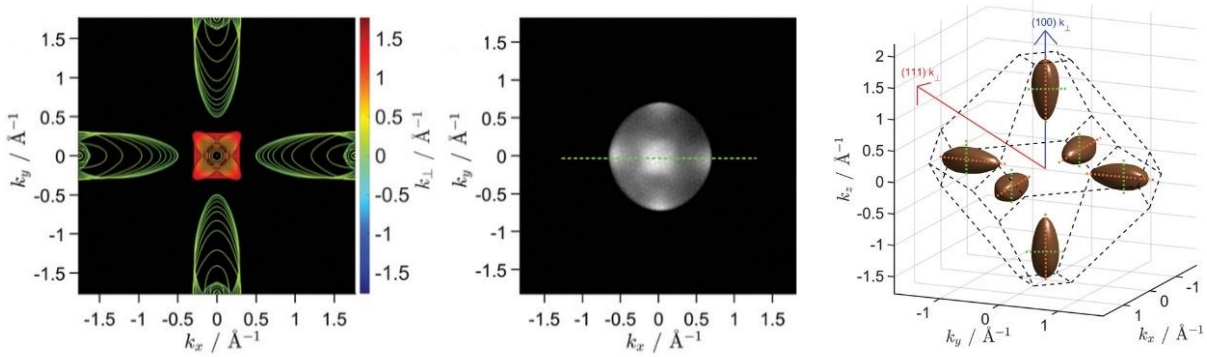

Fig. 1. Calculated (left) and experimental (center) secondary emission spectroscopy isoenergetic cut close to the CBM for a diamond (100). 3D reconstruction (right) of the empty states close to the diamond CBM.[1]

[1] G. Wan … M. Cattelan, Advanced Functional Materials, **4**, 2007319 (2021)
[2] G. Wan, M. Cattelan et al. Carbon, **185**, 376 (2021).