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Theoretical study of the conductivity of ZnO through hydrogenation of ZnO surfaces

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Abstract – Zinc Oxide is a very studied material because of its large technological applications. There are several works that show an important n-type conductivity in ZnO bulk, that has been lately attributed to hydrogen impurities. In this work we study ZnO surfaces, and observe a metallic character of the ZnO surface after hydrogenation, dependent however on the hydrogen coverage.

ZnO is a material of large importance in a wide range of technological applications [1,2] , such as photocatalysis, solar cells, gas sensors , bio and optical devices. Several theoretical studies about ZnO bulk have been done lately [1,3-5]. In particular, it is observed an important n-type conductivity, that has been attributed to hydrogen impurities in the bulk.

In this study we are interested in the reactivity of ZnO surfaces to hydrogen exposure, using for that ab-initio DFT calculations in the local density approximation (LDA) and ultrasoft pseudopotentials, with the Espresso Code.

We find that the degree of contamination, or coverage of hydrogen atoms is important to determine the electronic properties of the surface. Figure 1 shows a stable configuration for the $(10\bar{1}0)$ surface partially saturated with external (figure 1a) (ZnO $(10\bar{1}0)$ (2x1):Hext) and internal (figure 1b) (ZnO $(10\bar{1}0)$ (2x1):Hint) hydrogen atoms. In both configurations we observe an increase of the metallicity of the surface. The PDOS plots (figure 2) show the metallic character of the ZnO surface after hydrogenation (ZnO $(10\bar{1}0)$ (2x1):Hext). However this behaviour is not found for the completely saturated surface (ZnO $(10\bar{1}0)$ (2x1):2H). Figure 2 also shows that the hydrogen states for the partially saturated surfaces are completely delocalized over the valence band and *reach up to the valence band top* while for the totally hydrogenated surface the hydrogen behaviour is the opposite.

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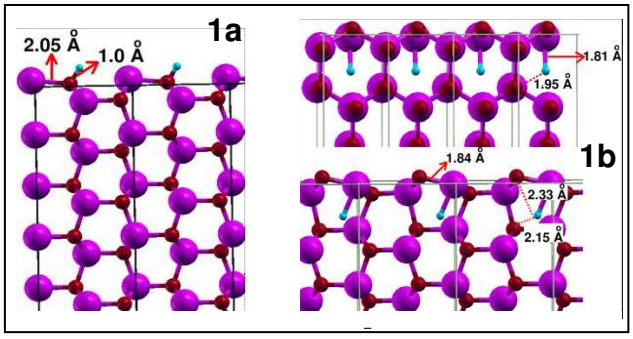

Figure 1: Hydrogenated **a)** ZnO $(10\bar{1}0)$ (2x1):Hext and **b)** ZnO $(10\bar{1}0)$ (2x1):Hint metallic surfaces.

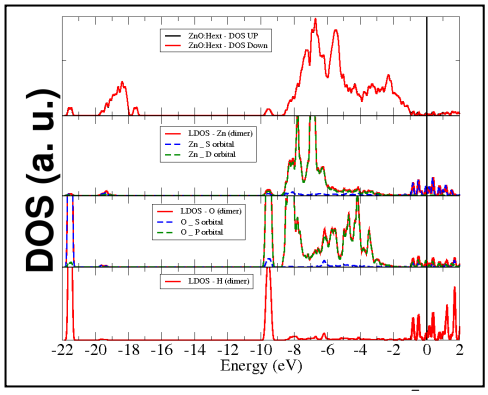

Figure 2: The PDOS plots of the ZnO $(10\bar{1}0)$ (2x1):Hext surface. See specially the delocalization of the hydrogen states over the valence band of the surface, reaching up the valence band top.

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