

Phase transition modulation of VO₂ film by hydrogenation in acid solution

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Hydrogenation is an effective way to tune the property of metal oxides. It could conventionally be performed by doping hydrogen atoms into solid materials with noble metal catalysis, high-temperature/pressure annealing treatment or high energy proton implantation in vacuum condition. Acid solution naturally provides a rich proton source, but according to the common wisdom it should cause corrosion rather than hydrogenation to metal oxides. Here we report a strikingly simple approach to hydrogenate monoclinic vanadium dioxide (VO₂) in acid solution at ambient condition by placing a small piece of low workfunction metal (Al, Cu, Ag, Zn or Fe) on VO₂ surface. It is found that the attachment of a tiny metal particle (~1.0mm) can lead to the complete hydrogenation of an entire wafer-size VO₂ (>2 inch). Moreover, with the right choice of the metal a two-step insulator-metal-insulator phase modulation can even be achieved. An electron-proton co-doping mechanism has been proposed and verified by the first principles calculations, and confirmed in experiment of electron-Li⁺ co-doping into VO₂. This non-catalytic hydrogenation approach offers a conceptually new atomic doping technique for VO₂ materials.

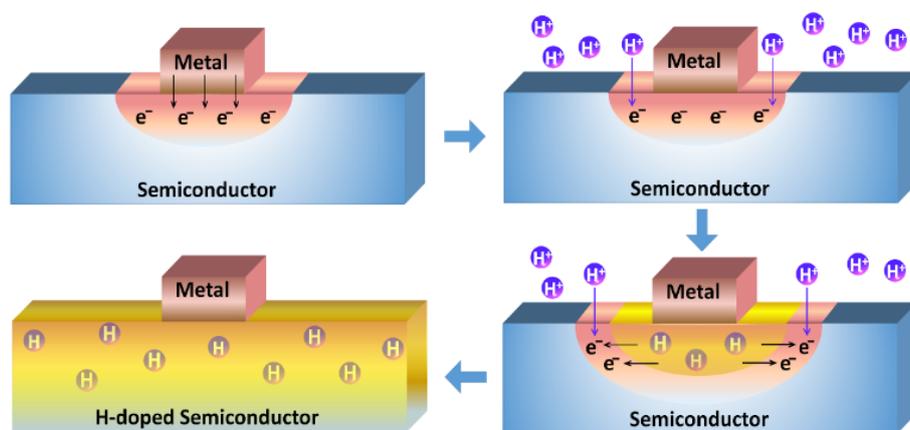


Figure. The schematic illustration of the contagious electron-proton co-doping mechanism with the metal-acid treatment to semiconductor: (1) Electrons flow to semiconductor when the metal contacts VO₂ film. (2) Once the metal/VO₂ is immersing into acid solution, chemical reactions go sequentially as (a) $M-x[e^-] \rightarrow M^{x+}$, (b) $VO_2+x[e^-]+x[H^+] \rightarrow H_xVO_2$. Here protons penetrate to meet electrons, creating conductive H-doped structure. Meanwhile the attached metal (M) is gradually dissolved in acid to become M⁺ cations for balancing charges in solution. (3) Electrons flow from conductive H-doped structure to the un-doped parts, driving more proton penetration. (4) The repeated “electron flowing–proton penetration–phase transition–electron further flowing” cycle expands toward full H-doping.