Topic number: 3 and/or 4

OXYGEN-VACANCY SUPERLATTICES IN α-Fe_2O_3 NANOSTRUCTURE DUE TO PLASMA OXIDATION

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Despite many important applications of α-Fe_2O_3 in semiconductors, catalysis, sensors, clinical diagnosis and treatments, two fundamental mechanisms that are crucial to these applications remain theoretically unexplored– (I) long range and periodic oxygen-vacancy ordering in the planes of $(3\bar{3}0)$ and $(1\bar{1}2)$ (Chen et al. [1]), and (II) the relationship between the oxygen vacancies and the electronic transition from *n*- to *p*-type conductivity (Lee et al. [2]). Nevertheless, the properties of oxygen ordering and superlattices was first studied in $La_3(Ni,Co)_2O_5$ by Vidyasagar et al. [5].

Creation of such vacancies in α-Fe_2O_3 were possible due to an innovative and universal approach proposed by Cvelbar et al. [3]. In this technique, the synthesis of α-Fe_2O_3 nanowires and nanobelts were carried out by direct plasma oxidation of bulk Fe materials. This method was originally proposed by Mozetič et al. [4] to synthesize high-density niobium oxide nanowires. Here, we give unambiguous theoretical justifications in order to explain why and how (A) long range ordering of oxygen vacancies occur in the planes of $(3\bar{3}0)$ and $(1\bar{1}2)$, (B) the vacancies are periodic, namely, for every tenth (or fifth) plane for $(3\bar{3}0)$ and for every fourth plane for $(1\bar{1}2)$ and (C) the *n*-type semiconductor, α-Fe_2O_3 electronically transformed into a *p*-type semiconductor.

We make use of the ionization energy theory [6] and its renormalized ionic displacement polarizability functional [7] to show that (a) the periodic oxygen-vacancy ordering is the initial step prior to random oxygen diffusion out of α-Fe_2O_3, (b) the most likely mobile plane is indeed $(1\bar{1}2)$, while the oxygen vacancies in the plane $(3\bar{3}0)$ is actually referring to the oxygen vacancies in the $(1\bar{1}2)$ plane by symmetry. The mobility of the plane is determined from the polarizability of oxygen with respect to $Fe^{2+,3+}$ and non-clustering property of oxygen, (c) the frequencies of periodicity (1/10, 1/5 and 1/4) are entirely due to the temperature and concentration (oxygen) gradient and (d) the *n*- to *p*-type conductivity transition is solely due to the polarizability of iron as a result of oxygen vacancies.

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