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CALCULATION OF ELECTRONIC PROPERTY CHANGES IN Zn-DOPED α-SiO_2 USING DENSITY FUNCTIONAL THEORY

Annotation. *In this study the Vienna Ab-initio Simulation Package (VASP 6. 5) with the Heyd–Scuseria–Ernzerhof 2006 (HSE06) hybrid functional was used to calculate the variation in the electronic density of states and band gap of α-SiO_2 upon Zn doping using density functional theory (DFT). For undoped silicon dioxide calculations showed a band gap of 9. 06 eV. The band gap dropped to 0. 839 eV when Zn was added at a concentration of 8. 33 percent in relation to silicon atoms. According to an analysis of the electronic density of states the hybridization between the O p-valence orbitals and the Zn d-valence orbitals was responsible for this band gap narrowing. This led to a shift in the valence band and the formation of new electronic states within the forbidden gap. According to the obtained results Zn incorporation into α-SiO_2 increases the materials sensitivity to light in the infrared spectrum and induces semiconductor-like characteristics in terms of band gap energy. The theoretical basis for the possible use of Zn-doped SiO_2 in semiconductor materials sensors photocatalysts and optoelectronic device technologies is provided by these findings.*

Key words:*VASP, HSE06, Silicon dioxide, PBE, TDOS, PDOS*

ZICHLIK FUNKSIONAL NAZARIYASI ASOSIDA Zn KIRITILGAN α -SiO_2 NING ELEKTRON XOSSASIDAGI O‘ZGARISHLARNI HISOBLASH

Annotatsiya.*Ushbu tadqiqotda zichlik funksional nazariyasi (DFT) asosida rux (Zn) kiritilgan α-SiO_2 materialining elektron holatlar zichligi va taqiqlangan zona kengligidagi o‘zgarishlarni hisoblash uchun Heyd–Scuseria–Ernzerhof 2006 (HSE06) gibrid funksionali bilan Vienna Ab-initio Simulation Package (VASP 6.5) dasturidan foydalanildi. Doplanmagan kremniy dioksid uchun hisoblashlar natijasida ta-*

qiqlangan zona kengligi 9.06 eVga teng ekani aniqlandi. Zn atomi kremniy atomlariga nisbatan 8.33 % konsentratsiyada kiritilganda, taqiqlangan zona kengligi 0.839 eVgacha kamaydi. Elektron holatlar zichligi tahliliga ko'ra, kislorodning p-valent orbitallari bilan ruxning d-valent orbitallari orasidagi gibridlanish ushbu zona torayishiga sabab bo'lgan. Natijada valent zona siljishi va taqiqlangan zonada yangi elektron holatlarning hosil bo'lishi kuzatildi. Olingan natijalarga ko'ra, Zn ning α-SiO_2 tarkibiga kiritilishi materialning infraqizil spektrda yorug'likka sezgirligini oshiradi hamda taqiqlangan zona energiyasi nuqtai nazaridan yarimo'tkazgichga xos xususiyatlarni yuzaga keltiradi. Ushbu natijalar Zn bilan doplangan SiO_2 ning yarimo'tkazgich materiallar, sensorlar, fotokatalizatorlar va optoelektron qurilmalarda qo'llanilishi uchun nazariy asos bo'lib xizmat qiladi.

Kalit so'zlar: *VASP, HSE06, kremniy dioksid, PBE, TDOS, PDOS.*

РАСЧЁТ ИЗМЕНЕНИЙ ЭЛЕКТРОННЫХ СВОЙСТВ A-SIO_2 ЛЕГИРОВАННОГО ЦИНКОМ ZN НА ОСНОВЕ ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИ

Аннотация. *В данной работе с использованием теории функционала плотности (DFT) были выполнены расчёты изменения электронной плотности состояний и ширины запрещённой зоны α-SiO_2 при легировании цинком (Zn) с применением пакета Vienna Ab-initio Simulation Package (VASP 6.5) и гибридного функционала Heyd–Scuseria–Ernzerhof 2006 (HSE06). Для нелегированного диоксида кремния расчёты показали ширину запрещённой зоны 9.06 eV. При добавлении Zn в концентрации 8.33 % по отношению к атомам кремния ширина запрещённой зоны уменьшилась до 0.839 eV. Анализ электронной плотности состояний показал, что гибридизация между p-валентными орбиталями кислорода и d-валентными орбиталями цинка является причиной сужения запрещённой зоны. Это приводит к смещению валентной зоны и формированию новых электронных состояний внутри запрещённой зоны. Согласно полученным результатам, внедрение Zn в α-SiO_2 повышает чувствительность материала к свету в инфракрасной области спектра и придаёт ему полупроводниковые свойства с точки зрения ширины запрещённой зоны. Полученные результаты создают теоретическую основу для возможного применения Zn-легированного SiO_2 в полупроводниковых материалах, сенсорах, фотокатализаторах и оптоэлектронных устройствах.*

Ключевые слова: *VASP, HSE06, диоксид кремния, PBE, TDOS, PDOS.*

Introduction. Silicon dioxide (SiO_2) as a the primary component in silicon-based semiconductor technology plays a crucial role in electronics and optoelectronics due to its high electrical insulating properties, chemical stability, and wide band gap (~9.0 eV). However, these same properties limit the ability to tune its electrical conductivity and optical spectrum. Doping SiO_2 with a variety of metals, such as transition metals, has been the subject of numerous studies with the objective of regulating its electronic, optical, and magnetic properties [1,2].

In recent years, there has been an increasing interest in the modification of SiO_2 with zinc (Zn) atoms. Zn-doped SiO_2 materials have been thoroughly investigated thanks to their valuable light-emission characteristics, photocatalytic efficacy, and vast applicability in sensors [3]. Previous theoretical analyses have mainly considered the influence of Zn on crystalline SiO_2 phases, exemplified by α-quartz. DFT calculations have been applied in prior studies to assess the electronic and optical properties of $ZnSiO_3$ and Zn_2SiO_4 [5]. Formation energy calculations show that Zn can occupy substitutional and interstitial sites in SiO_2, enabling Zn incorporation and Zn–O–Si bond formation [5]. Despite progress, significant gaps remain. Computational studies often provide limited analysis of doping effects in SiO_2, and the configuration-dependent impact of Zn on its electronic band structure is largely unexplored. Data are also scarce on Zn clustering during doping and the defect states that may result. Here, we use density functional theory (DFT) within the Vienna Ab initio Simulation Package (VASP) to examine in detail how Zn doping influences the electronic properties of SiO_2.

Calculation approach. The calculations were performed using the Vienna Ab initio Simulation Package (VASP 6.5) with the Projector Augmented Wave (PAW) method parameterized by Perdew, Burke, and Ernzerhof (PBE) within the Generalized Gradient Approximation (GGA). For band gap calculations, the Heyd–Scuseria–Ernzerhof 2006 (HSE06) hybrid functional was employed. The plane-wave cutoff energy was set to 480 eV. For geometry optimization, a force convergence criterion of 0.02 eV/Å and an energy convergence criterion of 1×10^{-5} eV were applied. Sampling of the Brillouin zone was carried out using a $3 \times 3 \times 5$ Γ-centered k-point mesh for both the pristine and Zn-doped supercell configurations [7, 8, 9, 10]. Calculations for SiO_2 in its undoped and Zn-doped states were performed according to the above parameters.

Results and discussion. The unit cell was initially optimised from a 9 × 9 × 5 Γ-centred k-point mesh for Brillouin zone sampling of α-SiO_2. The optimized lattice parameters of the unit cell were found to be a = 4.97 Å, b = 4.97 Å, and c = 5.48 Å for α-SiO_2. The calculated lattice parameters exhibited strong correlation with the experimental values reported in [11]. In consideration of the findings, the construction of the supercell was initiated and Zn doping was incorporated into subsequent calculations (see Figure 1).

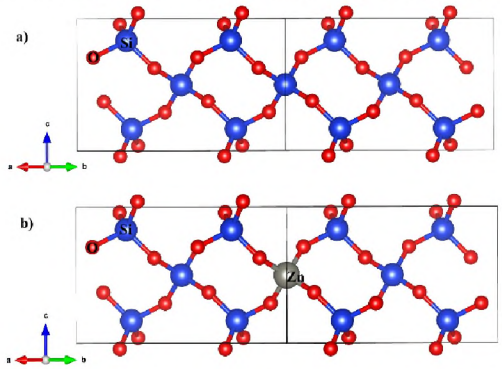


Figure 1. Structural visualization of α-SiO_2 in the (a) undoped and (b) Zn-doped states.

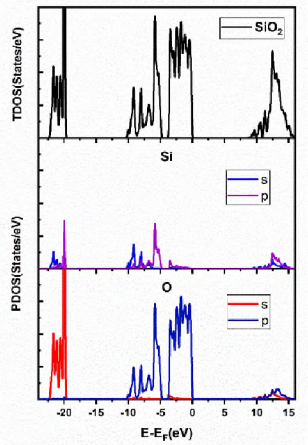


Figure 2. Total (TDOS) and partial (PDOS) density of states of pristine α-SiO_2 (before Zn doping).

Initially, the total and partial density of states were calculated for the undoped system. The results indicate that in the lower valence band region, the electronic states are predominantly derived from the oxygen valence s-orbitals. In the upper valence band region, the oxygen p-orbitals are the primary contributors to the electronic states. This observation suggests that oxygen serves as an electron acceptor. In the proximity of the Fermi level, a reduction in the electronic states derived from the silicon p-orbitals is observed, thereby indicating that silicon undergoes an electron loss (see Figure 2).

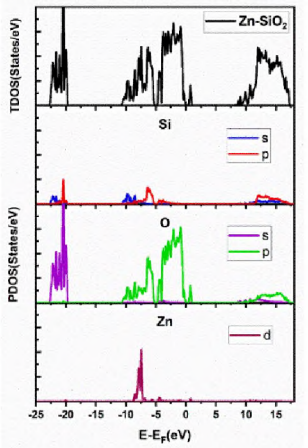


Figure 3. Total (TDOS) and partial (PDOS) density of states of α-SiO_2 after Zn doping.

The doping of Zn into SiO_2 has been shown to cause significant alterations in both the total (TDOS) and partial (PDOS) density of states. It has been established that an additional, low-intensity electronic state emerges in the upper valence band, with this state predominantly originating from oxygen p-orbitals and

with a significant contribution from Zn valence d-orbitals. This Zn-induced state has also been observed to shift the oxygen p-orbital distribution in the upper valence band (see Figure 3).

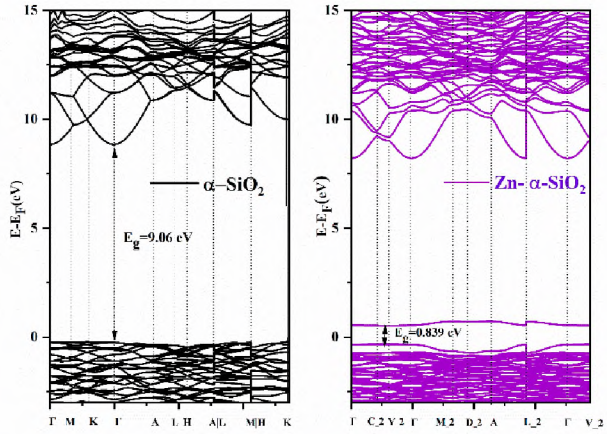


Figure 4. Band structure of α-SiO_2 in the undoped and Zn-doped states.

The band structure of α-SiO_2 was analyzed in both its pristine state and with 8.33% Zn doping, relative to the number of silicon atoms. For undoped α-SiO_2, calculated using the HSE06 hybrid functional with a 45% Hartree–Fock exact exchange component, the band gap was 9.06 eV. Zn incorporation reduced the gap dramatically to 0.839 eV, indicating a substantial alteration of the electronic structure. Total and partial density of states (DOS) analyses confirmed that this reduction arises from hybridization between Zn valence d-orbitals and O p-orbitals, which generates an additional electronic level within the gap. The presence of this mid-gap state suggests enhanced electronic activity, potentially enabling transitions at much lower energies (Figure 4).

Conclusion. The density of states and band gap of α-SiO_2, before and after Zn doping, were calculated using density functional theory. For pristine α-SiO_2, the band gap was 9.06 eV, whereas the introduction of Zn at 8.33% (relative to the number of Si atoms) reduced it sharply to 0.839 eV. DOS analysis attributed this narrowing to hybridization between Zn valence d-orbitals and O valence p-orbitals, producing a mid-gap state through a shift in the valence band.

Zn incorporation thus transformed α-SiO_2 into a semiconductor with enhanced infrared light sensitivity. These modifications highlight the potential of Zn-doped SiO_2 for applications in semiconductor devices, sensors, photocatalysts, and optoelectronic systems.

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