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Estimation of the charge state of Th implanted in SiO₂ in the different atomic environment

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Abstract. In this work the investigation of the charge states of thorium implanted in SiO₂ is in different atomic environments and at different concentrations is presented. Th was considered as interstitial and substitutional impurity in model cells of 6, 48 and 96 atoms. The estimations of the Bader effective charges of Th was derived from the electronic charge density $n(\mathbf{r})$ calculated in DFT full relativistic PAW pseudopotential approximation. The change in the electron density of thorium due to the environment in the cells was estimated in comparison with the free atomic state.

1. Introduction

The ²²⁹Th nucleus has a unique low-lying isomeric level in the excitation spectrum, the energy of which is currently estimated at 8.10 +/- 0.17 eV [1]. Intensive experimental [2-5] and theoretical [6-20] studies of the last 30 years have revealed a number of unusual properties in this nuclear state associated with the peculiarities of the interaction of the nucleus with its own electron shell and chemical environment. Among them are decay through an electron bridge and excitation in a laser plasma, the influence of boundary conditions on the lifetime of a level, conversion on conduction electrons in a metal, relatively fast alpha decay, a test of the exponentiality of the basic law of radioactive decay of an isolated state, the relative effects of the variation of the fine structure constant and the strong interaction parameter and others.

One of the most interesting feature is dependence of the decay from the electronic shell's charge state in Th atom. In the [14-15] was shown that in Th ions, implanted in the wide-gap dielectric, excited ^{229m}Th nuclei relaxes in the ground state by the gamma radiation. In this way, the electron-conversion channel is fully suppressed due to the energy prohibition. Mentioned property of the nuclear transition allows to create the time and frequency standard with the fractional frequency stability of 10⁻¹⁹ – 10⁻²⁰



[16-18] and the coherence gamma VUV (gamma-laser) of 150-160 nm wavelength[19-20]. Thus, the investigations of the excited state $^{229m}\text{Th}(3/2+, 8.1 \text{ eV})$ is highly actual for the modern fundamental science and technologies both.

For the prospective investigations and technological applications the experimental schemes wished to allow to separate the processes of the different decay channels and lifetimes or suppress one of them. In [21] was proposed a solid-state based conception utilizing implantation of excited ^{229}Th into thin silicon oxide layers and measuring the excitation energy and lifetime of the isomeric state using an electronic spectrometer. If the excited ^{229}Th ions are implanted into a wide-gap dielectric ($> 8 \text{ eV}$), then the prompt electronic internal conversion process is blocked, and isomer lifetime expected to be increased by minutes [3]. An experimental scheme for measuring the single photon energy during the decay of an isomeric thorium-229 nucleus implanted in a wide-gap VUV dielectric. It allows measurement of the energy of photons in the ultraviolet (UV) range using an electronic spectrometer. The proposed method utilizes thin silicon oxide layers obtained by thermal oxidization of the pure silica wafers, Th ions implanted inside by pulse laser implantation. Within this solid-state framework, the optimization of the system parameters is carried out, the study of the energy levels of the implant in the "trap" in SiO_2 , including through theoretical calculations and computational experiment.

In this work the quantum-based calculations of the cells modeling the atomic nearest-neighbor environment surround Th implanted in SiO_2 . The density functional theory (DFT) approach including relativistic effects was used and self-consistent charge density was analyzed by the Bader method and soft [22, 23]. The changes of the electron density of the Th electronic subsystem due to the surrounding, with respect to the single state. Estimation of the Th effective charge in the different environments can help one to detect the minimal consistent model for the former electronic band structures and spectra calculations to study the Th implant's fine-structure levels in the local trap in SiO_2 .

2. Model cells and calculations approaches

According to the [21] the thin silicon oxide layers obtained by thermal oxidization of the pure silica wafers is used as substrate material. In its structure present the structural SiO_4 -tetrahedrons like in cristobalite and quartz. Meanwhile the cristobalite density 2.3 g/sm^3 is closest to the amorphous modification, thus it is widely used as a model substitution or the first approximation of the amorphous one [24]. To estimate the Thorium effective charge we took in account only the nearest atomic surrounding, in case of any concentrations of Th in substrate. As a surrounding model we use the unit cells, illustrated in the Figure 1.

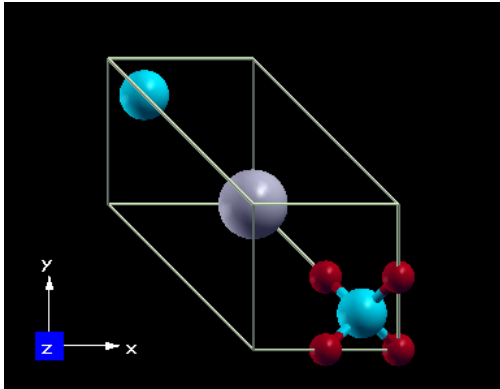


Figure 1.1 FCC model cell of SiO_2 with 6 atoms and 1 Th interstitial impurity. Si, O – blue and red bells, Th – violet bell.

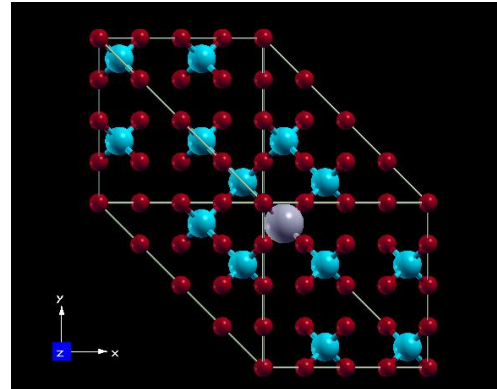


Figure 1.2. FCC model cell of SiO_2 with 48 atoms where 1 Th substituted Si.

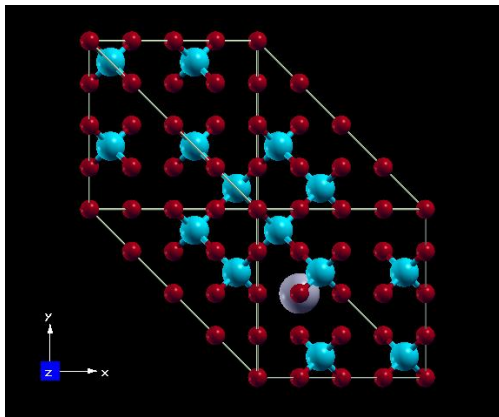


Figure 1.3. FCC model cell of SiO_2 with 48 atoms and 1 Th interstitial impurity.

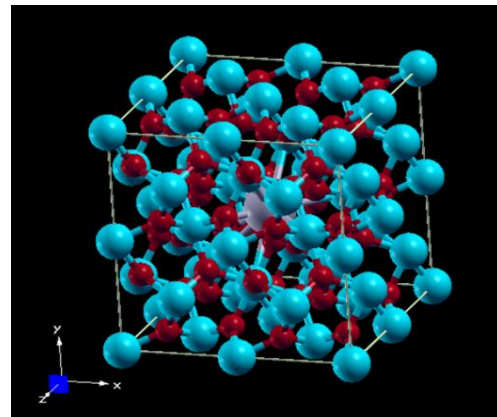


Figure 1.4. Cubic model cell of SiO_2 with 96 atoms and 1 Th substituted Si.

The one of the primitive FCC cells SiO_2 consists of the 6 atoms Si, O, and 1 Th implanted in the interstitial space (Figure 1.1). Second FCC cell contains 48 Si and O atoms, and 1 implanted Th (Figure 1.2). In the same 3rd cell Th substitutes one of the Si atom (Figure 1.3) and locally one can see the thorium oxide-like formation. 4th cubic cell contains 96 atoms where Th substitutes one of the central Si atom (Figure 1.4).

For described cells the self-consistent electronic density $n(\mathbf{r})$ was calculated using projector augmented-wave (PAW) pseudopotential method implemented in Quantum Espresso soft [25]. Exchange and correlation effects were treated with DFT generalized-gradient approximation Perdew-Burke-Ernzerhoff (PBE) functional [26]. Pseudovalence states was determined including valence and deeper subvalence states within fully relativistic PAW (PBE) pseudopotentials Si (3s2 3p2), O (2s2 2p4), Th (6s2 7s2 6p6 6d1 5f1) [27, 28]. As in self-consistent problem only those states was included, less number then Z but more than chemical valence, we will name it “pseudovalence”. Self-consistent calculation was performed on the k -points (0 0 0) и (0 0.5 0) of the irreducible 1st Brillouine zone for FCC cells and k -points (0 0 0) and (0.5 0.5 0.5) for cubic. Planwave energy cutoff 1500 eV.

3. Thorium effective charge states in Si and O environment

Define changes in thorium electron density due to the surrounding in cells with respect to the free atomic state as N_{eff} . N_{eff} measured in e units is $N_{\text{eff}} = N_{\text{pseudo}} - N_{\text{bader}}$, where N_{pseudo} is the number of the pseudovalence electrons of Th defined in pseudopotential (12). N_{bader} is the effective number of a pseudovalence electrons associated with Th, surrounded by Si and O, derived from the self-consistent density of cells $n(\mathbf{r})$ by the Bader method. N_{eff} can be considered as effective charge or ionicity. Effective charges N_{eff} of Th is shown in Table 1.

Table 1. Thorium charge states in model cells Th:SiO₂

Th:SiO ₂ model cell	N_{pseudo}	N_{bader}	$N_{\text{eff}} = (N_{\text{pseudo}} - N_{\text{bader}})$
6+1 FCC (Th interstitial impurity)	12.0	11.0	1.0
48+1 FCC (Th interstitial impurity)	12.0	11.2	0.8
48 FCC (Th substitutional impurity)	12.0	6.9	5.1
96 cubic (Th substitutional impurity)	12.0	7.2	4.8

From the data in Table 1 one can see that Th as substitutional impurity tends to loss the electron density (N_{eff} 4.8 and 5.1), that is likely because Th substituting Si appears to be locally surrounded by the 4 O atoms, and then by the structural tetrahedrons SiO₄ (see Fig.1). But in the e units charge loss of Th is greater than O neighbor's number — 4. This configuration can approximately describe an ionized Th implantation (in the real process), in the stadium of relaxation in the pore, between lattice nodes or in substitution position. In the case of Th implantation between the structural tetrahedrons SiO₄ (in Fig.1.1-1.2) effective electronic density of Th decreases as well, nearly by 1e (N_{eff} 1.0, 0.8). Also the calculated effective electrons loss decreases as the model cell increases.

The described approach was used as a preliminary estimation of the environment models, determination of the minimum consistent unit cell for further studies of the fine structure using more detailed calculations. It can be assumed from the results obtained that cells of 48-96 atoms may be sufficient for further investigation of the band structure and electronic spectra of the system of Th ions introduced into the SiO₂ matrix, and the corresponding Th concentration in the sample - for studying the kinetics of implantation.

Acknowledgments

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