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A DFT Study of the Components of a Hf/HfO$_2$/TiN three-layer stack

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Abstract

In the present study, the unit cells of metallic Hafnium (Hf), Hafnium Oxide (HfO$_2$), and Titanium Nitride (TiN), which are the components of a novel Hf/HfO$_2$/TiN three-layer stack with great potential for applications in nanoelectronics, are theoretically described by employing the plane wave pseudopotential approach as implemented in the Vienna *Ab Initio* Simulation Package (VASP). All the calculations are performed within the Generalized Gradient Approximation (GGA) by adopting the Perdew-Burke-Ernzerhof (PBE) functional. As a result of the present study, a systematic procedure for the quantum-mechanical simulation of each system is proposed as follows: (i) construction of the model from experimental data, (ii) determination of the optimal value of the plane wave energy cutoff, (iii) optimization of the parameter that defines the number of k-points in the reciprocal space, and (iv) geometry optimization of the cell parameters and atomic positions. In the specific case of the HfO$_2$ system, on-site Coulomb corrections (GGA+U method) are applied to calculate an accurate energy band gap value.

Keywords. DFT, PBE, on-site Coulomb corrections, band gap

Resumen

En el presente estudio, las celdas unitarias del hafnio metálico (Hf), óxido de hafnio (HFO$_2$), y nitruro de titanio (TiN), que son los componentes de una interfaz innovadora de tres capas: Hf/HFO$_2$/TiN, que posee gran potencial para aplicaciones en nanoelectrónica, es descrita teóricamente mediante la aproximación de pseudopotenciales y ondas planas como se encuentra implementado en el Paquete de Simulación *Ab Initio* de Vienna (VASP). Todos los cálculos se realizan usando la Aproximación del Gradiente Generalizado (GGA), con el funcional de Perdew-Burke-Ernzerhof (PBE). Como resultado del presente estudio, se propone un procedimiento sistemático para la simulación mecánico cuántica de cada sistema, resumido de la siguiente manera: (i) la construcción del modelo a partir de datos experimentales, (ii) determinación del valor óptimo de la energía de corte para las ondas planas, (iii) optimización del parámetro que determina el número de puntos k en el espacio recíproco, y (iv) la optimización de la geometría de las posiciones atómicas y de los parámetros de celda. En el caso específico del HfO$_2$, se aplica el método de correcciones coulómbicas localizadas (GGA+U) para calcular un bandgap de energía más exacto.

Palabras Clave. DFT, PBE, correcciones Coulombicas, brecha de bandas electrónicas

Introduction

Inorganic chemistry and material science has played an important role in the development of semiconductor industry due to the fact that parts in semiconductor applications like high-κ dielectrics gate stacks are made from perovskites and metal oxides [1]. One important application of semiconductors are information memory storage, and advances in this field require the development of novel materials [2]. An interesting field of research is the development of nonvolatile memories, and among them, resistance random access memories (RRAM), which are metal-insulator-metal gate stacks that store information through the switching of the insulator resistance [3].

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One of the possible components used for RRAM gate stack fabrication, is the TiN/Hf/HfO$_x$/TiN resistive element stack, where the top and bottom metallic electrodes are made of TiN. The insulator layer is made of HfO$_2$, that is one of the most interesting high-κ dielectric material with a permittivity laying in the 20-25 range [4]. The Hf layer of the stack acts as an oxygen buffer, favoring the formation of oxygen-deficient HfO$_2$, which allows filament creation for resistance switching [5].

In this work, a quantum mechanical study focused on the properties of metallic Hf, TiN and the insulator HfO$_2$ is presented as a preliminary effort to theoretically investigate the properties of the Hf/HfO$_2$/TiN gate stack at the atomic-electronic level with the purpose of study the switching resistance behavior of the layer stack.

In the next section, we begin describing briefly the DFT calculation methods implemented within the Vienna *ab-initio* simulation package (VASP). Then, a procedure is established to determine optimal values for some computational parameters as the energy cutoff and the k-point mesh parameter, in order to perform an accurate geometry optimization of the primitive cell parameters in comparison with experimental values. As some DFT functionals (*i.e.* PBE) underestimate the value of the energy band gap in insulator materials, on-site Coulomb corrections are applied in HfO$_2$ to solve this issue.

Methodology

Density Functional Theory

The fundamental problem in the description of electronic structure of materials is to solve the Schrödinger equation of a many-electron system in the presence of a nuclei field. According to the Born-Oppenheimer approximation, the kinetic energy of the nuclei is neglected and the nucleus-nucleus interactions can be considered constant. Thus the Schrödinger equation for a system consisting of N nuclei with constant coordinates $\vec{R} \equiv \vec{R}_1, \ldots, \vec{R}_N$ and N_e electrons with coordinates defined as $\vec{r} \equiv \vec{r}_1, \ldots, \vec{r}_{N_e}$ is simplified as

$$\left[T_e + V_{ee}(\vec{r}) + V_{Ne}(\vec{r}, \vec{R})\right] \Psi(\vec{r}) = E\Psi(\vec{r}), \qquad (1)$$

where T_e is the kinetic energy of electrons, V_{ee} is the electron-electron repulsion and V_{Ne} is the nucleus-electron interaction. The many-electron wave function $\Psi(\vec{r})$, is a function of $3N_e$ variables, which contains all the dynamic information of the electrons of the system.

Since the Schrödinger equation of many-electron systems is difficult to solve, alternative methods have been developed for the quantum-mechanical description of molecules and crystals. Density functional theory (DFT) offers an alternative approach to solve the many-body problem, where the properties of a system are determined through functionals of the electron density $n(\vec{r})$. According to the Hohenberg-Kohn theorems (*i.e.* the fundamental theorems of DFT): (i) the energy of the system is a unique functional of the electronic density and (ii) the correct ground state electronic density minimizes the energy functional, and the resulting energy is the ground state energy. Therefore, the ground state density of the original interacting system can be parameterized in terms of a set of one-electron orbitals (i.e., Kohn-Sham orbitals), representing a non-interacting reference system where all the many-body terms are incorporated into an exchange-correlation functional E_{XC}.

One of the approaches of DFT to determine E_{XC} is the local-density approximation (LDA), where the unknown functionals are approximated by the corresponding energies of a homogeneous electron gas having the same local density. Other common approach is the generalized gradient approximation (GGA), which takes into account the local density and the gradient of the density at some point [6].

It is known that DFT functionals as LDA or GGA underestimate the energy band gap in insulators, because they are not accurate describing systems with strongly correlated electrons. This inaccuracy has been solved by introducing an intra-atomic interaction known as on-site Coulomb corrections [14]. Within the GGA or LDA approach, this method is known as GGA+U or LDA+U respectively.

Procedure for geometry optimization

As we are interested in describing the electronic properties of conducting materials such as Hafnium and Titanium Nitride (together with the insulator Hafnium Oxide are components of Hf/HfO$_2$/TiN three-layer stack), the plane wave approach is required for the construction of the electronic wave function of these systems [6]. Taking this into account, the Vienna *Ab Initio* Simulation Package (VASP) is used to perform the computational calculations [7]. For all simulations, the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [8] is adopted, and the interaction between ions and electrons is described by non-conserving projector augmented wave (PAW) pseudopotentials [9, 10]. A procedure for the quantum mechanical simulation of each primitive cell is proposed below:

Step 1. Construction of the primitive cell models. In order to build the models of the primitive cell of each system, we obtain the cell parameters from experimental data. In the Hf/HfO$_2$/TiN layer stack it is known that HfO$_2$ is formed by atomic layer deposition (ALD) at 300 K, being constituted especially of amorphous and monoclinic phases. After annealing the stack at 1000 K, poly-crystalline HfO$_2$ is the common phase observed in thin films. The three crystalline polymorphs are the monoclinic, tetragonal, and cubic phases. Among these three phases, the monoclinic one is stable at low temperature [11]. In this work we choose a monoclinic HfO$_2$ primitive cell, because it is one of the most studied

Element	Structure	Space Group	Wyckoff position	Site symmetry	Coordinates
Hf	hexagonal	$P6_3/mmc$ (194)	2c	-6m2	(1/3,2/3,1/4) (2/3,1/3,3/4)
HfO_2	monoclinic	$P2_1/C$ (14)	4e	-1	(x,y,z) (-x,y+1/2,-z+1/2) (-x,-y,-z) (x,-y+1/2,z+1/2)
TiN	cubic	Fm-3m (225)	4a	m-3m	(0,0,0)

Table 1: Wyckoff positions of primitive cells

and reported phases in literature [5]. A topic of further investigation is the modeling of the stack using polycrystalline HfO_2. In the other hand, for pure Hf and TiN elements, an hexagonal and a cubic primitive cells have been chosen, respectively. The Wickoff positions and coordinates of the atomic positions for each element are shown in Table 1 [12].

Step 2. Energy cutoff optimization. In order to determine the optimal value of plane wave energy cutoff, single point energy calculations were performed in each primitive cell with cutoff energies ranging from 100 to 800 eV. For the electronic self consistent process, a high accuracy break condition of 1×10^{-7} eV is used. The optimal value for the energy cutoff is considered the point where the total energy remains constant with respect to the energy cutoff value.

Step 3. K-point mesh parameter optimization. To perform the optimization of the parameter that defines the number of k-points in the reciprocal space, it is used the corresponding energy cutoff previously obtained for each primitive cell. Then single point energy calculations are performed with k-points meshes ranging from $2 \times 2 \times 2$ to $18 \times 18 \times 18$. In all simulations the Brillouin zone for the bulk geometry is sampled in meshes of k-points generated through the Monkhorst-Pack scheme. For the electronic self consistent process, a high accuracy break condition of 1×10^{-7} eV is used. The optimal value for the k-point mesh parameter is considered the point where the total energy remains constant with respect to the parameter value.

Step 4. Geometry optimization. Geometry optimization of cell parameters and ion positions is performed together with an optimization of the width of the smearing (sigma). We varied the sigma parameter from 0.02 eV to 2.0 eV. The width of the smearing is optimized using the criterion that the calculated entropy of the system must be less than 1 meV/atom for each primitive cell. For the Brillouin zone integration of the primitive cells, the Gaussian smearing method is used for HfO_2 as it is an insulator and the smearing method of Methfessel-Paxton is used for Hf and TiN, as these are metallic compounds.

To carry out the ionic relaxation of each primitive cell, the values of energy cutoff and k-point mesh parameter obtained from the last optimizations are used. The relaxations are performed using automatic cell shape and volume optimization from VASP. The ions are moved into their instantaneous groundstate using a conjugate-gradient algorithm [13]. In all cases, symmetry of each primitive cell was kept.

Band gap calculation

In the stack under investigation, two layers are conducting materials (TiN and Hf), and the middle layer is made of an insulator (HfO_2). For the former layers we can compare the computed lattice parameters with the experimental values to validate the accuracy of the PBE functional in describing the materials. In the other hand, for the HfO_2, besides lattice parameters we must check if the energy band gap is in accordance with experimental values.

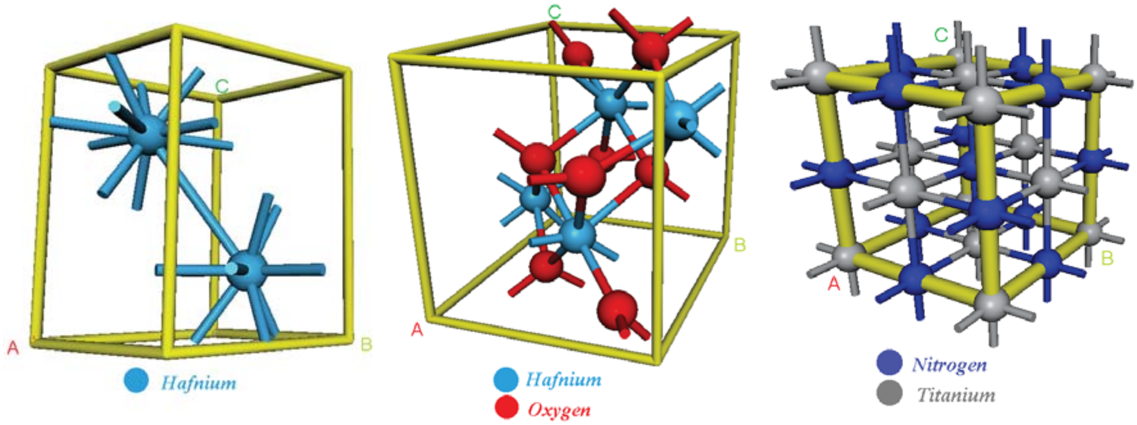
In order to calculate the energy band gap of the HfO_2 primitive cell, a single point energy calculation is performed on the equilibrium geometry, using the tetrahedron smearing method with Blöchl corrections, which is recommended for high accuracy electronic relaxations. The energy band gap is calculated from the density of states vs. total energy plot, as the difference between the bottom of the conduction band and the top of the valence band.

It is well known that traditional DFT functionals such as PBE underestimate the energy band gap in insulators, because these functionals are not accurate in the description of systems with localized strongly correlated d and f electrons. This lack of accuracy of the DFT functionals has been solved by introducing a strong intra-atomic interaction in a screened Hartree-Fock approach, known as on-site Coulomb interaction [14]. Within the generalized gradient approximation approach, this method is known as GGA+U. In this work, a simplified approach as proposed by Dudarev is used [15], where only the difference between the on-site interaction energy U and the exchange parameter energy J is considered meaningful in the energy functional.

Thus, on-site Coulomb corrections are applied in the HfO_2 to improve the calculation of the energy band gap. In the present study, the corrections applied are 4 eV for Hafnium $5d$ orbital and 28 eV for Oxygen $2p$ orbital. These values have been determined empirically from previous DFT calculations and have shown to be the optimal ones for the HfO_2 system to obtain an energy band gap and lattice parameters in good agreement with the experimental values [16].

Results and Discussion

In the following we present the results of implementing the procedure proposed in the last section in order to



(a) Hexagonal Hf **(b)** Monoclinic HfO_2 **(c)** Cubic TiN

Figure 1: Models of primitive cells.

model and optimize the geometry of each element of the Hf/HfO_2/TiN layer stack. Models of each primitive cell are shown in Figure 1.

Hafnium Hf

For the hexagonal pure Hafnium primitive cell, an optimal energy cutoff of 240 eV has been found. The optimization of the parameter that determines the k-ponits has given a $11 \times 11 \times 11$ mesh. The energy convergence for energy cutoff and k-point mesh parameter can be seen in Figures 2 (a) and 3 (a). After performing the geometry optimization of the primitive cell using GGA functional, the value of the width of the smearing that satisfied the required criterion for the entropy was 0.08 eV. The errors calculated for each cell parameter with respect to experimental values were small. We had an overestimation of 0.09% in a and b parameters and 0.10% for c parameter.

To obtain an accurate energy bang gap for HfO_2, on-site Coulomb corrections were applied on Hf and O orbitals; therefore, a new geometry optimization under GGA+U functional was performed on Hf primitive cell for consistency. After the ionic relaxation the cell parameters of Hf were overestimated by 3.58% in a and b parameters, and 3.80% for c parameter. The results for the geometry optimization together with the error respect to the experimental parameters are shown in Table 2.

Variation in cell parameters using GGA and GGA+U functionals could be explained by the fact that the on-site Coulomb interaction is set as potential energy to keep two electrons on the same atomic site, which encourages electron/hole localization on atoms. In this case, the calculated GGA+U $5d$ orbitals of Hafnium are slightly more localized than that predicted by GGA. Therefore an increment in the Hf primitive cell is expected.

Hafnium Oxide HfO_2

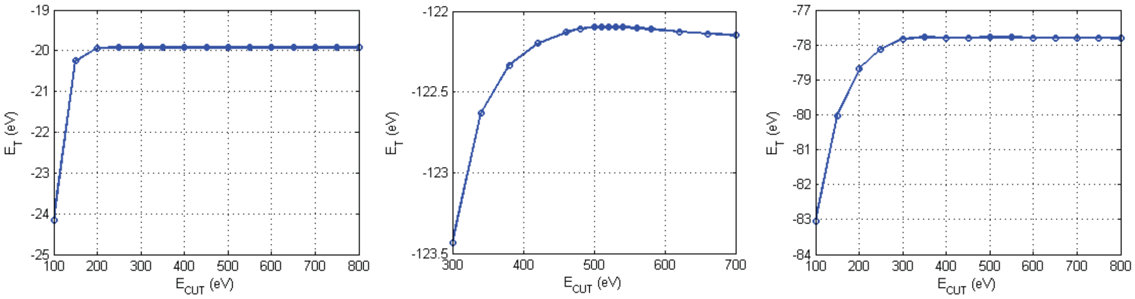
For the monoclinic insulator Hafnium Oxide primitive cell, an optimal energy cutoff of 515 eV was found. The optimization of the parameter that determines the k-ponits has given a $8 \times 8 \times 8$ mesh. The energy convergence for energy cutoff and k-point mesh parameter can be seen in Figures 2 (b) and 3 (b).

After the geometry optimization of the primitive cell using the GGA functional, the sigma value that satisfied the required criterion for the entropy was 0.08 eV. The errors calculated for each cell parameter with respect to experimental values give an underestimation of 0.52% in a parameter, 0.39% in b parameter and 0.69% in c parameter. The β angle had a small underestimation of 0.23%.

The energy band gap of HfO_2 primitive cell was calculated from the density of states plot obtaining a value of 4.16 eV, as can be seen in Figure 4. This energy band gap is below the reported experimental values of 5.6 to 5.8 eV for monoclinic HfO_2 [17], [18]. This result was expected since the traditional DFT functionals underestimate the value of band gaps in insulators. Consequently on-site Coulomb corrections (GGA+U) were applied for HfO_2 components, specifically to Hafnium $5d$ and Oxygen $2p$ orbitals.

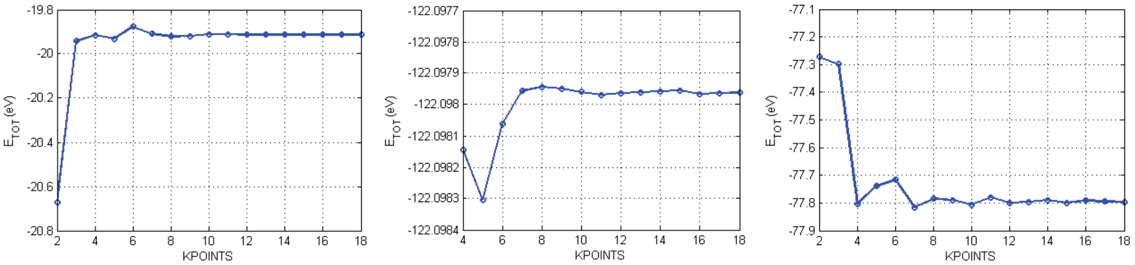
After the ionic relaxation with the GGA+U functional, the cell parameters of HfO_2 were underestimated by 0.07% in a parameter, 1.70% in b parameter and 0.76% in c parameter. The β angle had a small overestimation of 0.08%. In the case of HfO_2, it is noticed that the overestimation in lattice parameters is given specially along b-direction. The results for the geometry optimization and the errors in comparison to the experimental parameters are shown in Table 2.

The energy band gap of HfO_2 primitive cell was calculated obtaining a value of 5.80 eV, as shown in Figure 5. This energy band gap is in agreement with the experimental values for monoclinic HfO_2. Therefore the use of on-site Coulomb corrections gave a more reliable value of band gap.



(a) Hf **(b)** HfO_2 **(c)** TiN

Figure 2: Energy cutoff optimization.



(a) Hf **(b)** HfO_2 **(c)** TiN

Figure 3: K-point mesh parameter optimization.

Element		a (Å)	b(Å)	c(Å)	α(°)	β (°)	γ (°)
Hf	Experimental	3.1964	3.1964	5.0511	90	90	120
	GGA	3.1936	3.1936	5.0459	90	90	120
	Error (%)	0.09	0.09	0.10	0	0	0
HfO_2	Experimental	5.1170	5.1733	5.2910	90	99.2200	90
	GGA	5.1435	5.1936	5.3277	90	99.4437	90
	Error (%)	-0.52	-0.39	-0.69	0	-0.23	0
TiN	Experimental	4.2720	4.2720	4.2720	90	90	90
	GGA	4.2514	4.2514	4.2514	90	90	90
	Error (%)	0.48	0.48	0.48	0	0	0
Hf	Experimental	3.1964	3.1964	5.0511	90	90	120
	GGA+U	3.3109	3.3109	5.2431	90	90	120
	Error (%)	3.58	3.58	3.80	0	0	0
HfO_2	Experimental	5.1170	5.1733	5.2910	90	99.2200	90
	GGA+U	5.2202	5.1459	5.3475	90	99.2197	90
	Error (%)	-0.07	-1.70	-0.76	0	0.08	0
TiN	Experimental	4.2720	4.2720	4.2720	90	90	90
	GGA+U	4.2514	4.2514	4.2514	90	90	90
	Error (%)	0.48	0.48	0.48	0	0	0

Table 2: Lattice parameters for geometry optimization.

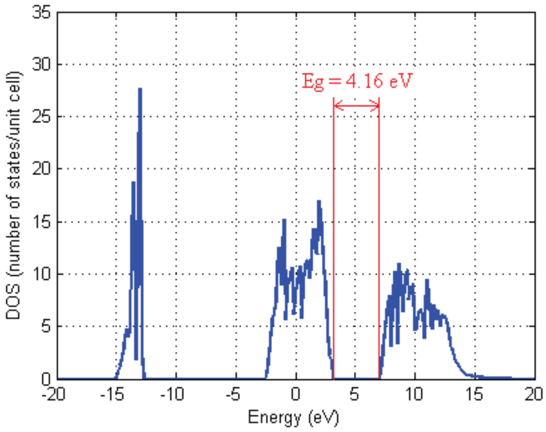


Figure 4: **Density of states and bandgap of HfO_2 calculated using GGA method.**

Titanium Nitride TiN

For the cubic TiN primitive cell, we have found an optimal energy cutoff of 450 eV and a mesh of 11 × 11 × 11 k-points. The processes of optimization are shown in Figures 2 (c) and 3 (c).

After computing the geometry optimization of the primitive cell using the GGA functional, the error calculated for the cell parameter has given an underestimation of 0.48%. For TiN no change has been reported when performing the geometry optimization using GGA+U functional due to the fact that no Coulomb corrections has been applied in Nitrogen or Titanium orbitals. The results for the geometry optimization together with the errors with respect to the experimental parameters are shown in Table 2.

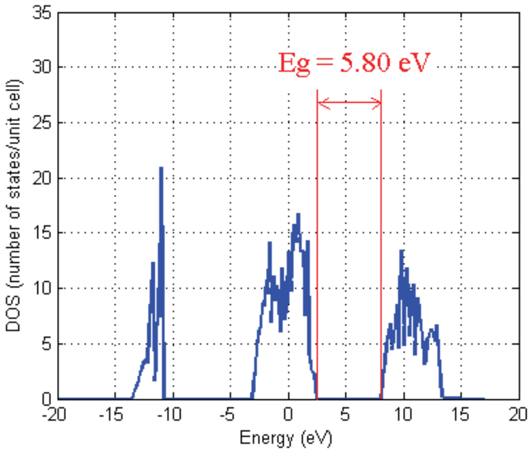


Figure 5: **Density of states and bandgap of HfO_2 calculated using GGA+U method.**

Primitive cell	E_{cut} (eV)	K-points
Hf	240	11 × 11 × 11
HfO_2	515	8 × 8 × 8
TiN	450	15 × 15 × 15

Table 3: **Optimized values of energy cutoff and k-point mesh parameter.**

Conclusions

Using density functional theory under the generalized gradient approximation functional for exchange an correlation, the elements of a Hf/HfO_2/TiN three-layer stack have been modeled, obtaining primitive cells for hexagonal Hf, monoclinic HfO_2 and cubic TiN. The procedure proposed in this work has been applied to optimize the energy cutoff and the k-point mesh parameter, performing single point energy calculations for each primitive cell. In the geometry optimization of the Hf and HfO_2 primitive cells, it has been shown that applying of on-site Coulomb corrections (GGA+U method) on d-Hafnium and p-Oxygen orbitals improves the energy band gap of HfO_2, from 4.16 eV calculated using GGA method, to 5.80 eV calculated using GGA+U method. However, this method of calculation results in a small expansion in the cell parameters, specially in Hf primitive cell. This computational optimization based on DFT will be used to further investigate on the electronic properties of the Hf/HfO_2/TiN layer stack, in order to study the resistance switching effect under an electric field.

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