

# Ab initio calculations of aluminium clustering on aluminium surfaces

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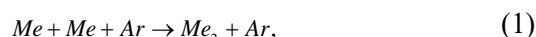
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**Abstract :** Aluminium (Al) nanofilms have been extensively used as interconnection wires, electrodes, and other components in nanoelectronics. In this paper, elementary processes of Al atom clustering on aluminium substrate are considered and corresponding ab initio calculations are performed with the ABINIT package in frames of the density functional theory (DFT). Structure geometries of aluminium clusters  $Al_N$  ( $N=1-5$ ) on the single crystal most packed faces (100), (110), and (111) surfaces were obtained. The calculation scheme was tested on free clusters  $Al_N$  ( $N=1-5$ ), bulk aluminium and the most packed faces (100), (110), and (110) of the aluminium single crystal. The computed bond energies and lengths are in good agreement with the experimental data and results of other authors. The basic processes of the magnetron film formation by small aluminium clusters were considered. The presented results provide some preliminary data essential for a microscopic description of the aluminium nanofilm formation in the magnetron sputtering process at low-pressure argon plasma and in similar processes favoring small cluster deposition. We consider microscopic conditions that determine a primary mode of aluminium thin-film growth (layer-by-layer, island formation, or layer-plus-island). We show that small cluster deposition may be a perspective well-controlled method for production of high-quality single crystal Al nanofilms.

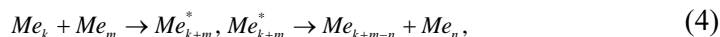
Keywords: small metal clusters, magnetron film formation, aluminium, density functional theory, ABINIT;

## 1. Introduction

Presently, magnetron sputtering (MS) is one of the main thin film deposition methods widely adopted in nanoelectronics production. MS allows to get films with higher adhesion and homogeneity than evaporation deposition [1], without heating of the target. Development of the sputtering method has generated a considerable interest in nanostructure synthesis of clusters and nanoparticles. A number of methods to produce the structures have been developed [2–6]. Standard MS in an inert gas (argon, pressure of 0-1 mbar) allows to obtain small clusters mainly with dominant intensities at 1 – 4 atoms [7,8]. Instead of argon other inert gas may be used as the sputtering gas, but the following consideration holds true. Large cluster condensation may be induced by Ar, but such processes are rare and special sputtering setup should be used with long enough path of the target atoms to the substrate. An increase of the cluster size may be produced by addition of helium [8]. High energy ejected target atoms ( $Me$ ) may be cooled by inert gas atoms according to reactions



Process (2) is more effective than process (1) because at the same transferred momentum a helium atom transfers ten times the energy transferred by an argon atom ( $m_{Ar}/m_{He}=10$ ). Probability of the sequence (3) decreases then the  $Me$  mass increases, for the same reason. Obviously, this probability increases with the growth of the metal atom concentration in plasma. Further clustering is effected by way of a following sequence:



Therefore, short path from the target to the substrate and one-component heavy inert gas favor small clusters, deposition of bigger clusters may be negligible. For example, intensities  $I$  of  $Ar^+$  clusters



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produced by sputtering with argon (0.4 mbar) decrease from  $I_1 \approx 450$  pA;  $I_2 \approx 300$  pA;  $I_3 \approx 950$  pA;  $I_4 \approx 250$  pA to  $I_N < 100$  pA for  $N > 4$  [8].

In this paper we consider deposition of small aluminium clusters ( $Al_N$  ( $N=1-5$ )) on the aluminium (100), (110), and (110) surfaces in frames of the density functional theory [9,10]. These elementary processes are essential for microscopic understanding of nanofilm deposition by magnetron sputtering then deposition of bigger clusters is negligible.

## 2. Methods

We performed DFT calculations of aluminium structures with ABINIT code [13–15] (Perdew-Burke-Ernzerhof generalized gradient approximation to the functional of the exchange-correlation energy [11,12]). We performed all geometry optimizations with recommended convergence criteria [16] for stresses, forces, energy cut off for the plane wave basis etc. The convergence of the unit cell binding energy was achieved with the accuracy of  $10^{-8} Ha$ .

## 3. Results and Discussion

Calculated ground state geometries of  $Al_N$  ( $N=3-5$ ) clusters (Fig. 1) illustrate changes of minimal bond lengths and may be used for qualitative analysis of a cluster fitting into a surface.

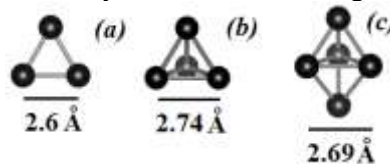


Fig. 1. Ground states of aluminium clusters.

We compare our calculation results with known experimental values and calculation results of other researchers in Table 1. We calculated also surface energies for the most packed faces:  $E_{(100)} \approx 0.407$  eV/atom  $\approx 0.795$  J/m<sup>2</sup>;  $E_{(110)} \approx 0.679$  eV/atom  $\approx 0.928$  J/m<sup>2</sup>;  $E_{(111)} \approx 0.862$  eV/atom  $\approx 1.924$  J/m<sup>2</sup>. The mean value  $\bar{E} = 1.216$  J/m<sup>2</sup>. These values are close to the experimental value of 1.143 J/m<sup>2</sup> [17], 1.169 J/m<sup>2</sup> [18]. The experimental values stem from the surface tension measured in the liquid phase and extrapolated to  $T=0$  K. Previously, surface energies were calculated with an approach close to our one:  $E_{(100)} \approx 0.86$  J/m<sup>2</sup>;  $E_{(110)} \approx 0.93$  J/m<sup>2</sup>;  $E_{(111)} \approx 0.67$  J/m<sup>2</sup> [19], with  $\bar{E} = 0.82$  J/m<sup>2</sup>. So our calculation overestimates the experimental data by about 5%, while previous calculation underestimated the data by about 30%.

Table 1. Calculated parameters of the  $Al_N$  clusters (ground states): dissociation energy per atom  $D_e$  and minimal bond lengths  $R_e$ . Values are compared with the experiment. The dissociation energy for bulk aluminium ( $Al_b$ ) was calculated from the enthalpy of the gaseous phase formation from the crystal phase at  $T=0$  K [21].

		$Al_2$	$Al_3$	$Al_4$	$Al_5$	$Al_6$	$Al_7$	$Al_8$	$Al_b$
$D_e$ (eV/N)	Our calc.	0.99	1.55	1.65	1.85	2.12	2.26	2.28	3.32
	Calc. [20]	0.83	1.39	1.61	1.80	2.07	2.16	2.16	
	Exp.	0.68 [20]	1.25 [20]						3.37 [21]
$R_e$ (Å)	Our calc.	2.46	2.60	2.74	2.69	2.73	2.60	2.65	2.91
	Calc. [20]	2.71	2.52						
	Exp.	2.7 [20]							2.86 [21]

Fulfilling all the preliminary computations, we calculated geometries (Figs. 2,3,4) and adhesion energies (Table 2) of small aluminium clusters ( $Al_N$  ( $N=1-5$ )) on the aluminium (100), (110), and (110) surfaces.

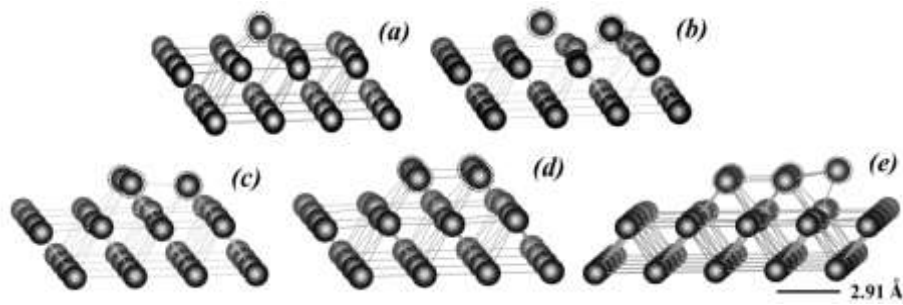


Fig. 2. Structures of aluminium clusters on the aluminium (100) surface. Cluster atoms are specified by dotted spheres.

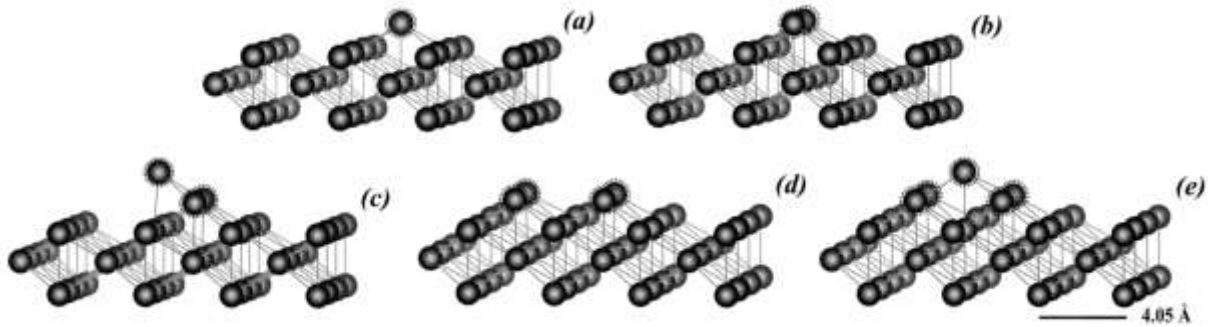


Fig. 3. Same as in Fig. 2 for (110) surface.

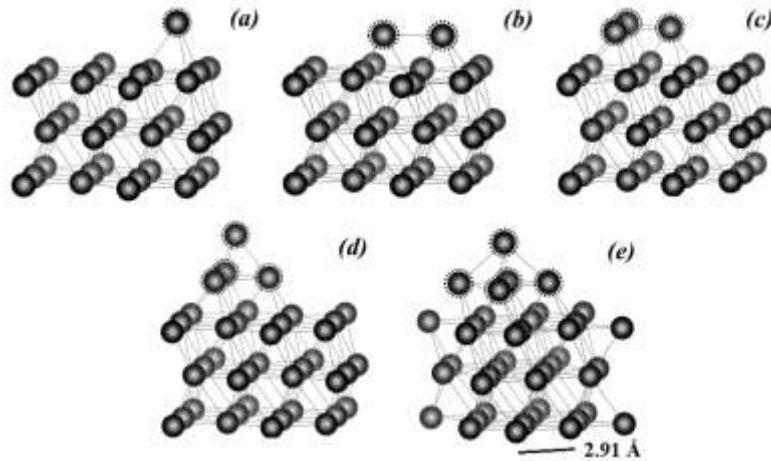


Fig. 4. Same as in Fig. 2 for (111) surface.

Table 2. Calculated adhesion energies  $E_N^{(xyz)}$  and  $E_N^{(xyz)}/N$  of  $Al_N$  clusters on the aluminium (xyz) surfaces.

$N$ (letter in Figs. 2–4)	$E_N^{(100)}$ , (eV)	$E_N^{(100)}/N$ , (eV/atom)	$E_N^{(110)}$ , (eV)	$E_N^{(110)}/N$ , (eV/atom)	$E_N^{(111)}$ , (eV)	$E_N^{(111)}/N$ , (eV/atom)
1 (a)	2.43	2.43	3.04	3.04	3.16	3.16
2 (b)	3.57	1.79	4.48	2.24	3.37	1.69
3 (c)	4.38	1.46	4.32	1.44	3.67	1.22
4 (d)	5.66	1.41	5.92	1.48	4.42	1.11
5 (e)	6.35	1.27	6.69	1.34	4.95	0.99

We consider a special conditions of magnetron sputtering then deposited clusters are cold (being in ground states) and small ( $N=1-5$ ). We also assume that cluster deposition is slow and energy surplus is dissipated by a thermostatic substrate. Table 2 allows us to analyze the  $Al$  film growth processes in three different cases of seed crystal orientation on the substrate. (A) For (100) surface parallel to the substrate (Fig. 2), the seed would grow with close rates in directions along the substrate and in the orthogonal direction for all deposited clusters. Such seed crystals form single crystal islands growing evenly in all directions. (B) For (110) surface parallel to the substrate (Fig. 3), growth in the orthogonal direction is preferable for all deposited clusters but  $Al_1$ . Such seed crystals form single crystal islands growing along a substrate more slowly than in the orthogonal direction. (C) For (111) surface parallel to the substrate (Fig. 4), growth in the directions along the surface is preferable for all deposited clusters

IOP Conf. Series: Journal of Physics: Conf. Series **1455** (2020) 012001 doi:10.1088/1742-6596/1455/1/012001 but  $Al_1$ . Such seed crystals form single crystal islands growing along a substrate more rapidly than in the orthogonal direction. We may stimulate growth in the direction orthogonal to the substrate by the monatomic deposition.

On a polycrystalline substrate, seed crystals are oriented randomly. According to our analysis an  $Al$  magnetron film grown on such substrate will be polycrystalline, variable in thickness: thicker for nanocrystals oriented as in (A), (B) and thinner for nanocrystals oriented as in (C). The mode of aluminium thin-film growth is island formation. In case of epitaxial film growth, the orientation of crystal seeds is mainly fixed and determined by the single crystal substrate [22]. A mode of aluminium thin-film growth is layer-by-layer formation for (C) orientation, and layer-plus-island formation for (A) and (B) orientations.

Considered problems form the basis for the subsequent investigation of the  $Al$ /magnetron nanofilm formation on non-aluminium substrates by small metal clusters. There are a number of different substrates that may be used. The nanofilms of least roughness should be single crystals. So substrate should be a single crystal as well. For instance, copper (001) thin film was epitaxially grown on the  $Al_2O_3$  (0001) substrate [22]. Presently we carry out numerical simulations and experiments with silicon substrates of different orientations.

#### 4. Summary

The presented calculation data show that there is a possibility to microscopically control the nanofilm deposition in the magnetron sputtering process at low-pressure argon plasma and in similar processes favouring small cluster deposition. The small cluster deposition may be a perspective well-controlled method for fabrication of high-quality single crystal Al nanofilms.

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