密度汎関数法による Cu(II)アセチルアセトナートの Cu(111)表面への吸着に関する検討 Density Functional Theory Study of Cu(II) Acetylacetonate Adsorption on Cu (111) surface

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Introduction

Atomic layer deposition (ALD) could deposit uniform and conformal thin films and is already applied to ultra-large-scale integration (ULSI) fabrication. An ideal ALD, in which a high degree of reproducibility and uniformity of the film thickness is guaranteed, requires the surface coverage is close to 1.0. From Langmuir isothermal, this means the product of adsorption equilibrium constant (K) and concentration of precursor on the surface (C) is much greater than 1 (usually KC > 10). Cu acetylacetonate (Cu(ACAC)₂) has been applied in both thermal ALD and Plasma-Enhanced ALD [1] for Cu film growth. Successful been made under depositions have various temperatures. Meanwhile, experimental and theoretical studies on surface chemistry and coverage are limited. Hu et al. studied the Cu(ACAC)2 surface chemistry on Cu (110) and indicated a possible dissociative path for the compound decomposed as Cu atom [2]. The loss of ACAC-ligands of the precursor has also been observed on Ni(110) and Cu (110) surfaces, and metal-Cu(ACAC) was formed. For more densely packed surface Cu (111), the adsorption of Cu(ACAC)₂ remains unclear. Recently, the density functional theory (DFT) calculation, has become a powerful tool to explicit the ALD chemistry at an atomic scale [3]. Herein, we focus on the adsorption of Cu(ACAC)₂ on Cu (111) by employing DFT calculations. Information like adsorption energy and adsorbed structure could be used to evaluate KC for current ALD performance, and to improve in the future. **Computation Details**

The optimized structure calculation for Cu(ACAC)₂ was carried out using Gaussian[@] 09 (Fig.1). The hybrid density functional theory B3LYP method with the 6-31G(d,p) basis set. The DFT adsorption calculations were performed using the Quantum Espresso (QE) package. The Kohn-Sham equations were solved by ultrasoft pseudopotentials. For the modeling of the exchange and correlation interactions, the Perdew-Burke-Ernzerhof (PBE) function was applied. Kinetic energy cutoffs of 340 eV (for wave functions) and 3061 eV (for charge density) were used. To understand the physisorption of the Cu precursor on the Cu (111) surface, a nonlocal van der Waals density functional (vdW-DF) was introduced in QE. The geometry was optimized until the total energy changes and all components of all forces are smaller than 1.36×10^{-5} eV. The Cu (111) surface is modeled with a period cell consisting of a 3 monolayers thick slab and a vacuum of 15 Å. Each monolayer is consisted of 36 Cu atoms, yielding a total of 108 Cu atoms for the whole slab. Multiple configurations are calculated and evaluated.

Result and Discussion

The adsorbed structure and energy were examined for three positions as shown in Fig.2. Position A is on top of the Cu atom, B is between two adjacent Cu atoms, and C is the center of the three Cu atoms located at the vertices of an equilateral triangle. The obtained adsorption structure and energy are consistent through these positions. The adsorption energy calculated of -1.215 eV is combined of -0.16 eV from PBE and -1.055 eV from vdW-DF, which indicates the adsorption calculated is physisorption. The small value from PBE indicates weak and insufficient interaction of orbital and electrons for precursor and surface. The difference of calculated physisorbed energy (-1.215 eV) with the energy (-1.34 eV) [2] on Cu (110) is possibly due to the more densely packed surface structure of Cu (111) compares with (110). From thermodynamics equilibrium, K could be calculated from temperature, adsorption energy, and change of entropies. The higher the adsorption energy, the higher the surface coverage when other conditions are fixed. In the future, we will further evaluate the chemisorbed energy and evaluate the performance of current ALD.



Fig 1. Cu(ACAC)₂ from Gaussian 09 (left); Adsorption structure of Cu(ACAC)₂ on Cu (111) surface (right)

Adsorbed Position	А	В	С
Adsorption Energy	-1.21 eV	-1.22 eV	-1.23 eV

Fig 2. Adsorbed positions and energies for A, B, and C are shown; white spots represent different adsorbed positions of Cu atoms in the Cu(ACAC)₂. Other geometries are the same.

Reference

[1] D. J. Hagen, M. E. Pemble, and M. Karppinen, *Appl. Phys. Rev.* 6, 041309 (2019)

- [2] X. Hu, J. Schuster, S. E. Schulz, and T. Gessner, *Chem. Chem. Phys.*, **2015**, 17, 26892 26902
- [3] Y. Maimaiti, S. D. Elliott, J. Phys. Chem. C 2015, 119, 9375– 9385,