

Adsorption and Surface Diffusion of Atomic Ru on TiN and SiO₂: A First-Principles Study

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Abstract: Ruthenium (Ru) has been suggested as one of the promising materials for nanoscale interconnects to substitute copper (Cu) that is currently used in the semiconductor industry. Through density functional theory (DFT) calculations, we present the rationales for varying deposition behavior of Ru on different types of substrates. For the SiO₂ and TiN substrates, with and without adsorbed hydrogen, our calculation results reveal the adsorption sites and their adsorption energy, the surface diffusion paths and their activation energy, and the surface diffusion coefficients. We confirm that the adsorption of Ru is more stable on TiN than on SiO₂ substrates, and that the surface diffusion of Ru adatom is faster on TiN than on SiO₂ surface.

Keywords: ruthenium; titanium nitride; silicon oxide; density functional theory; area-selective deposition

1. Introduction

Electronic devices have evolved into highly integrated low-power driving devices due to scaling down. Transistors have been continuously developed from a two-dimensional planar structure to three-dimensional structures such as FinFET and GAA (gate all around), whose minimal pitch size is approaching the thickness of tens of atoms. Accordingly, metal interconnects within such nanoscale electronic devices must also be fabricated at nm scale. The interconnect materials for the future semiconductor devices also have to satisfy the characteristics of thermal stability, good adhesion to substrates, low resistivity, high reliability, and ease of pattern formation [1,2]. By virtue of its low resistivity, copper (Cu) has been the widespread material for metallization of interconnects in semiconductor devices. However, diffusion of Cu through insulation layers can occur, requiring additional diffusion barrier layers such as TiN or TaN [3]. While the feature width of the interconnects has been scaled down in recent devices, the thickness of the diffusion barrier could not be reduced in accordance. In addition, as the width of the interconnects decreases, the current density within the interconnects increases, causing electromigration and a rapid increase in specific resistance. Furthermore, the electron mean free path of bulk Cu is large, such that when Cu is used with a linewidth of several nm, its specific resistance rapidly increases according to grain boundary scattering. Accordingly, research on various alternative interconnect materials whose specific resistance is less increased even at nanoscale linewidths is actively being conducted. Among them, ruthenium (Ru) may be a promising material due to its relatively shorter electron mean free path [4–6]. In addition, Ru may not require a diffusion barrier layer like Cu. Therefore, together with its higher melting point than Cu, Ru is considered an alternative nanoscale interconnect material.

On the other hand, achieving a high-aspect-ratio structure in the semiconductor fabrication process is highly challenging. To overcome such difficulty, the area-selective deposition (ASD) technique is being developed, which allows deposition to take place only on a specific, desired surface according to the difference in chemistry of the substrate surface via chemical vapor deposition (CVD) or atomic layer deposition (ALD) [7,8]. When it comes to the deposition of Ru, selectivity between SiO₂ and TiN substrates is often desirable,



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as the former is an interlayer dielectric (ILD) material preventing the metal wiring from interference, while the latter is deposited as a diffusion barrier for the metal into the ILD. Previous experimental studies have often shown that deposition of Ru exhibited more significant nucleation delay or island-type growth on SiO₂ substrates, whereas less nucleation delay and fast nucleation were achieved on TiN substrates [9–14]. While there is continuing debate on the underlying mechanisms that govern the deposition selectivity of Ru on different substrates, such as the adsorption chemistry of the precursors, differences in electronegativity, and differences in the interfacial energy, the relative rate of surface diffusion has been recently suggested to play a role [15–18]. Since strong dependence on the substrate materials is often observed during the initial nucleation of Ru thin films for either physical deposition methods such as sputtering and chemical deposition methods such as CVD or ALD [19–21], it can be suspected that surface-dependent adsorption is a significant fundamental property of Ru.

Surface and interface diffusion is crucial in a variety of applications including thin-film growth, fabrication of microelectronic devices, and material corrosion processes [22]. The rate of surface diffusion tends to be highly dependent on the temperature as enough thermal energy needs to be supplied to the diffusing atoms to overcome the activation energy barriers. The activation energy of surface diffusion, which needs to be overcome when the metal atoms diffuse from one adsorption site to another, can be modified when the type or condition of the substrate surface differs. Therefore, the surface diffusion rate, as well as its behavior, obviously depends on the substrate materials and their surface preparation conditions [23]. Atomistic simulations based on first-principles calculations are often shown to be powerful in estimating the diffusion coefficients [24,25], as recent studies on technologically important surfaces such as TiN and SiO₂ have shown [26–37].

In this study, we explored the adsorption and surface diffusion of atomic Ru on surfaces of TiN and SiO₂. With different substrate conditions regarding hydrogenation, we analyzed the difference in the adsorption and surface diffusion mechanisms using density functional theory (DFT). Our results quantitatively confirmed the deposition characteristics on each different substrates, indicating that deposition of Ru on TiN would be preferred over that on SiO₂.

2. Methods

Vienna ab initio simulation package (VASP) version 5.4.4 [38] was used for DFT calculations. The Perdew–Burke–Ernzerhof (PBE) functional [39] based on generalized gradient approximation (GGA) was used to calculate the electron density, together with the D3 method, applying Becke–Johnson damping for dispersion correction [40]. From benchmark studies in the literature, it is known that the performance of the PBE-D3 method toward the estimation of surface adsorption energies is comparable to other functionals [41,42]. To model the substrates, the most stable bulk structures of α -quartz SiO₂ (001) [43] and cubic TiN (100) [44] were obtained [45]. SiO₂ with full coverage of hydroxyls (OH) and TiN with 50% H coverage, where the hydrogen adatoms are present on top of the nitrogen sites, were additionally created. A vacuum of 15 Å was formed on the z-axis to optimize the slab structure. The SiO₂ substrate was optimized with a cutoff energy of 400 eV and Monkhorst-Pack k-point mesh of 3 × 3 × 1, while the TiN substrate was optimized with a cutoff energy of 450 eV and Monkhorst-Pack k-point mesh 5 × 5 × 1. The adsorption energy ΔE_{ads} , designated to the adsorption site for ruthenium atoms, was calculated using the following equation:

$$\Delta E_{ads} = E_{mole.ads} - (E_{slab} + E_{Ru}),$$

where $E_{mole.ads}$ is the ground-state energy in the state where a ruthenium atom is adsorbed on the slab surface, and E_{slab} and E_{Ru} represent the energy of each slab and ruthenium atom, respectively. The transition states for the diffusion process were analyzed using the climbing image nudged elastic band (CI-NEB) method [46] to evaluate the diffusion barrier

along the surface diffusion path of ruthenium atoms. The following relational expression was used for calculating the activation energy (E_a) for the surface diffusion:

$$E_a = E_{trans} - E_{mole.ads}$$

where E_{trans} is the transition state energy obtained from the CI-NEB calculation. The surface diffusion coefficient D can be calculated using the following equation [47]:

$$D = \frac{va^2}{4} e^{-E_a/k_bT},$$

where v is the jump frequency (assumed to be 10^{13} s^{-1}), a is the step distance (assumed to be 0.3 nm), k_b is the Boltzmann constant, and T is the deposition temperature.

3. Results and Discussion

Labeled with digits in Figure 1, the possible adsorption sites for Ru atoms are presented for the SiO_2 and TiN substrates. For the SiO_2 substrate, four different adsorption sites are identified: Si atom, O atom, Si–O bond, and hollow; the adsorption site at the Si–O bond is excluded for the hydroxylated SiO_2 substrate, since such a structure could not be properly optimized. Similarly, the TiN substrate, with or without hydrogen doping, provides four adsorption sites for ruthenium atoms: N atom, Ti–N bond, Ti atom, and hollow.

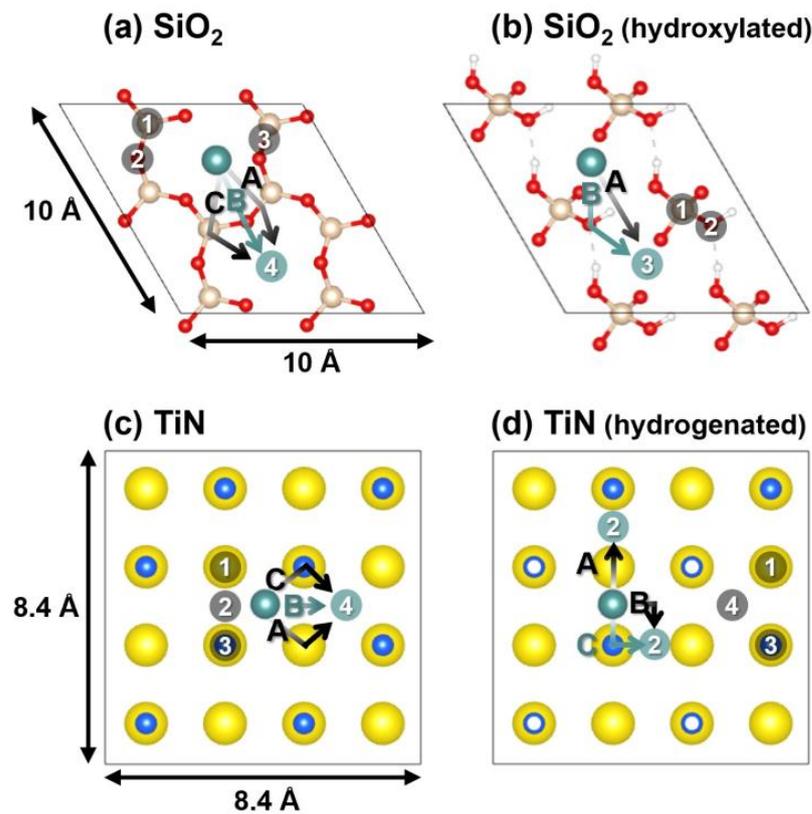


Figure 1. Available adsorption sites (labeled with digits, as defined in Table 1) and surface diffusion paths (labeled with letters) of ruthenium atoms on different substrates: (a) SiO_2 ; (b) hydroxylated SiO_2 ; (c) TiN; (d) hydrogenated TiN. The most stable adsorption sites and the most favorable surface diffusion paths are highlighted in turquoise. Ru = green, Si = tan, O = red, H = white, Ti = yellow, N = blue.

Table 1. Adsorption energy of Ru atom on each adsorption site as shown on Figure 1.

Substrate	Adsorption Site	Adsorption Energy (eV)
(a) SiO ₂	① Si atom	−0.61
	② O atom	−0.62
	③ Si-O bond	−0.61
	④ Hollow	−1.39
(b) SiO ₂ (hydroxylated)	① Si atom	−0.53
	② O atom	−0.43
	③ Hollow	−1.00
(c) TiN	① Ti atom	−2.98
	② Ti-N bond	−4.24
	③ N atom	−4.39
	④ Hollow	−4.47
(d) TiN (hydrogenated)	① Ti atom	−3.47
	② Ti-N bond	−4.65
	③ N atom	−4.45
	④ Hollow	−3.91

To find the most stable adsorption site for Ru adatoms, the adsorption energy ΔE_{ads} was calculated and compared for the different sites on each substrate (Table 1). The hollow site was confirmed as the most stable adsorption site for both pristine and hydroxylated SiO₂ substrates. The results also indicate that the other sites in the SiO₂ substrates were relatively unstable. While the pristine TiN substrate provided the lowest adsorption energy at the hollow site similarly to the SiO₂ cases, the hydrogenated TiN presented the most stable adsorption site at the Ti-N bond. This implies that the hydrogen doping may present an impact on the change in local atomic and electronic structures of substrate materials, which leads to the difference in the adsorption chemistry of ruthenium atoms. In addition, the TiN substrates exhibit about fourfold higher adsorption energy of ca. 4.5 eV than those on the SiO₂ substrates of ca. 1.2 eV. Such results suggest that the TiN substrates would show better adhesion characteristics for the Ru thin films [48], as well as preferential adsorption and deposition than the SiO₂ substrates, which corroborates previous experimental results.

On the basis of the analysis regarding the adsorption sites, the available paths of a Ru adatom for the surface diffusion are examined for each substrate as shown in Figure 1 (labelled with letters). The surface diffusion paths are assumed such that a Ru adatom on the most stable adsorption site diffuses to the closest identical adsorption site.

In Figure 2, the most favorable path is confirmed by calculating the activation energy E_a for the surface diffusion of a Ru atom. For both pristine and hydroxylated SiO₂ substrates, the lowest activation energy is achieved when the ruthenium atom diffuses over an oxygen atom. The pristine TiN substrate shows the minimal diffusion barrier for the diffusion across a Ti-N bond, while the hydrogenated TiN presents it for the diffusion over a nitrogen atom. By decreasing the activation energy, the hydrogen doping quantitatively changes the diffusion barrier of the ruthenium atoms on the SiO₂ substrates. Hydrogen-adsorbed TiN, on the other hand, shows smaller E_a for Ru diffusion compared to bare TiN, although the difference according to presence of H is only in the order of 0.1 eV. Overall, the E_a values for surface diffusion of Ru along the most favorable paths are significantly smaller on TiN substrates (0.1–0.2 eV) compared to SiO₂ substrates (0.5–0.9 eV).

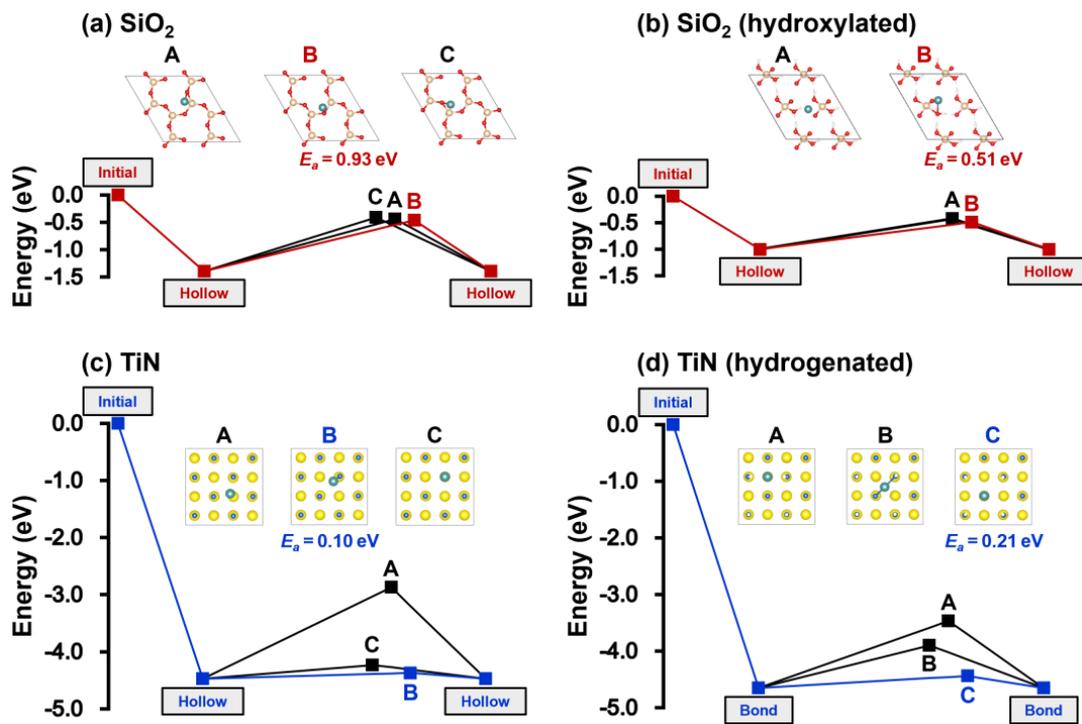


Figure 2. Diffusion energy diagrams of Ru atoms for each substrate: (a) SiO₂; (b) hydroxylated SiO₂; (c) TiN; (d) hydrogenated TiN. The most favorable surface diffusion path with its activation energy is highlighted in color for each substrate.

Figure 3 presents the calculated surface diffusion coefficients of Ru adatoms for each substrate over a range of temperature. The highest surface diffusion coefficient is achieved on the pristine TiN substrate, whereas the pristine SiO₂ substrate provides the lowest one, which is consistent with our discussion above, as well as the aforementioned experimental results. If both TiN and SiO₂ surfaces are covered by hydrogen adatoms, the surface diffusion coefficient of Ru is at least 200-fold larger on TiN than on SiO₂; if both surfaces are bare without H adatoms, the surface diffusion coefficient on TiN can be more than 5×10^6 -fold greater than that on the SiO₂ surface. The relative difference in the surface diffusion coefficients between SiO₂ and TiN substrates is large enough over typical temperature ranges for Ru ALD of around 450–650 K [49], such that the area-selective deposition of Ru may be accomplished by means of surface diffusion on substrates patterned with SiO₂/TiN.

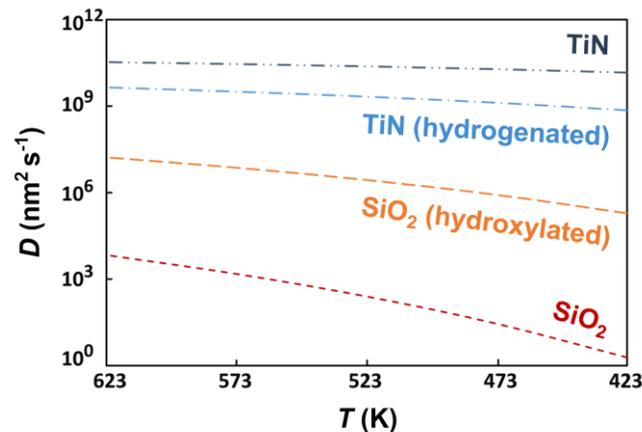


Figure 3. Calculated surface diffusion coefficients of Ru atoms for each substrate.

The analysis on the adsorption sites and their adsorption energy, the surface diffusion paths and their activation energy, and the surface diffusion coefficient enables us to suggest the rationales for different deposition natures of Ru on the SiO₂ and TiN substrates. The low surface diffusion coefficient of Ru for the SiO₂ substrates, which is derived from the high activation energy for the surface diffusion, can explain the island growth of Ru on them, while the opposite results are used to clarify how the layer-by-layer deposition is achieved on the TiN substrates.

In order to explore the electronic structures of the Ru-adsorbed substrates, the projected density of state (PDOS) of the most stable adsorption configurations of Ru on each surface is obtained, as summarized in Figure 4. While SiO₂ substrates are insulating with significant bandgaps (Figure 4a,b), the TiN surfaces indicate a metallic nature without a measurable bandgap (Figure 4c,d). It is found that the position of Ru orbitals on SiO₂ is dependent on the presence of H atoms on the surface, although the most stable adsorption site for Ru was determined for both bare and hydroxylated SiO₂ surfaces. On bare SiO₂, a sharp peak of the Ru 4*d* state is observed under E_F (Fermi level) of ca. −0.97 eV, while, on hydroxylated SiO₂, Ru 4*d* peaks at 1.25 eV above E_F. On the other hand, in the case of TiN, the Ru states are distributed over the range of ca. −2.5 to −1 eV under E_F, regardless of hydrogenation. Thus, there exists a fundamental difference in the chemical mechanism for adsorption of Ru adatom on SiO₂ and TiN surfaces, which may deserve future research attention.

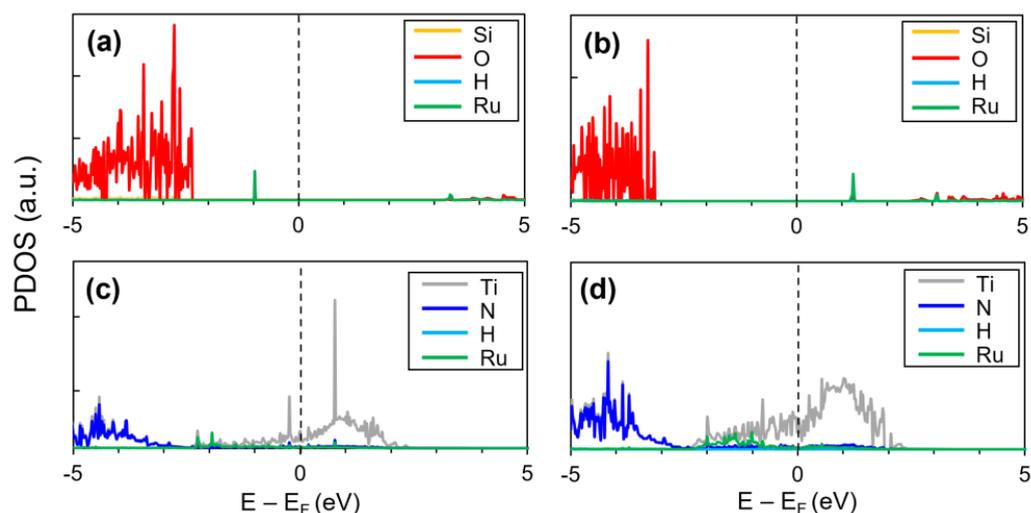


Figure 4. Projected density of states (PDOS) plots of the Ru adsorption structures on different substrates: (a) SiO₂ (hollow); (b) hydroxylated SiO₂ (hollow); (c) TiN (hollow); (d) hydrogenated TiN (Ti–N bond).

4. Conclusions

In this study, we analyzed the adsorption and diffusion behavior of ruthenium atoms on SiO₂ and TiN surfaces. DFT calculations were performed for the adsorption site-dependent adsorption energy, the activation energy dependent to surface diffusion paths, and the surface diffusion coefficient. We confirmed that the adsorption of Ru atoms is significantly more stable on the TiN substrates than the SiO₂ substrates regardless of pre-existing hydrogen, such that the adsorption energy of Ru on TiN is ca. fourfold larger than on SiO₂. Moreover, the surface diffusion of Ru on TiN is several orders faster than on SiO₂ surfaces. Our analysis can be used to explain the reported experimental results that the SiO₂ substrates often show island growth during Ru deposition, while the TiN substrates exhibit layer-by-layer deposition of Ru, as well as the finding that adhesion of Ru is stronger on TiN than on SiO₂.

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