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First-principles calculation of copper impurity diffusion in hexagonal ruthenium

S.A. Gorokhov[1,2]✉, A.A. Reznik[1,2], A.A. Rezvanov[1,2]

[1] Molecular Electronics Research Institute, Stock Company, Zelenograd, Russia;

[2] Moscow Institute of Physics and Technology (National Research University), Dolgoprudny, Russia

✉ sgorohov@niime.ru

Abstract. Ruthenium is a promising material for use in microelectronic devices as a diffusion barrier layer to prevent copper diffusion. However, there are few data on quantitative assessments of the diffusion coefficients of any impurities in hexagonal bulk Ru, which is the stable structural phase of Ru. In this work, we performed a density functional theory study of Cu impurity diffusion in bulk hexagonal Ru. Impurity diffusion coefficients are computed as a function of temperature using the '8-frequency model', which provides the relevant impurity and solvent jump frequencies and correlation factors. The effect of temperature-dependent expansion of the ruthenium lattice volume is taken into account within the quasi-harmonic approximation. The Arrhenius equation for the diffusion coefficient is $D_{\parallel} = 6.12 \cdot 10^{-5} \exp(-5.01 \text{ eV}/kT)$ m^2s^{-1} for diffusion within the basal plane and $D_{\perp} = 2.18 \cdot 10^{-4} \exp(-5.11 \text{ eV}/kT)$ m^2s^{-1} for diffusion between adjacent basal planes in the lattice. Our calculations serve as a foundation for a more accurate understanding of experimental data.

Keywords: impurity diffusion, diffusion coefficient, density functional theory, quasi-harmonic approximation, ruthenium, copper

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Моделирование диффузии примеси меди в гексагональном рутении из первых принципов

С.А. Горохов[1,2]✉, А.А. Резник[1,2], А.А. Резванов[1,2]

[1] Акционерное общество «Научно-исследовательский институт молекулярной электроники», г. Зеленоград, Россия;

[2] Московский физико-технический институт (национальный исследовательский университет), г. Долгопрудный, Россия

✉ sgorohov@niime.ru

Аннотация. Рутений является перспективным материалом для применения в микроэлектронике в качестве диффузионного барьерного слоя, предотвращающего диффузию меди. Однако диффузия каких-либо примесей в объеме гексагонального рутения теоретически мало изучена, и соответствующие коэффициенты диффузии отсутствуют в литературе. В данной работе проводится исследование из первых принципов диффузии примеси меди в объеме гексагонального рутения.

Ключевые слова: диффузия примеси, коэффициент диффузии, теория функционала плотности, квазигармоническое приближение, рутений, медь

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Introduction

One of the main trends in the modern semiconductor microelectronics industry is the continuous scaling down of minimum feature sizes [1]. Specifically, due to the narrowing of the width of copper conductors in the metallization system and reduction in the distance between them, there is active screening of new materials as diffusion barriers and adhesive layers for Cu. Metal ruthenium and its compounds are considered as potential materials for this application. Ru combines both high barrier properties, preventing Cu diffusion, and good adhesion to Cu [2].

In recent years, a substantial amount of research has been conducted on the development of diffusion barriers based on Ru. However, the methods of deposition used make it possible to obtain only polycrystalline films of Ru, in which Cu is expected to diffuse along the grain boundaries [3]. Consequently, such experimental studies do not provide information about the rate of diffusion of Cu in hexagonal (hcp) Ru. In this research, we perform a study of Cu impurity diffusion in bulk hcp Ru using the density functional theory (DFT) approach.

Methodology

For the calculation of vacancy-mediated diffusion coefficients of Cu in hcp Ru as a function of temperature the "8-frequency model" of Ghate was applied [4]. According to this approach, there are eight different jump frequencies corresponding to exchanges in the positions of impurity and nearest-neighbor solvent atoms with adjacent vacancies. Each of these eight jump frequencies was calculated based on the extended Eyring's equation [5] as

$$w = \frac{kT}{h}\exp\left(-\frac{G_{TS}^{*} - G_{IS}}{kT}\right), \tag{1}$$

where G_{TS}^{*} is the free energy of the transition state, which is a saddle point on the diffusion path, after excluding the contribution from its single imaginary phonon frequency, G_{IS} is the free energy of the initial state, h is Planck's constant, k is Boltzman's constant and T is absolute temperature. The resulting set of jump frequencies allows then to compute the correlation factor f and get diffusion coefficients

$$D_{\parallel} = \frac{3}{4}C_2 c^2 f_{Az} w_A, \tag{2}$$

$$D_{\perp} = \frac{1}{2}C_2 a^2 \left(3 f_{Bx} w_B + f_{Ax} w_A\right). \tag{3}$$

Here, C_2 is the vacancy adjacent to the impurity concentration defining through calculation of corresponding free energies, a and c are the lattice parameters of the hcp Ru, w_A and w_B are the jump frequencies of impurity and vacancy exchanges between adjacent basal planes and within a basal plane, respectively. In order to take into account the effect of thermal lattice expansion of ruthenium, a quasi-harmonic approximation (QHA) was applied preliminarily. Based on these results, four lattice parameters were obtained corresponding to temperatures of 300, 600, 900, and 1200 K for which diffusion coefficients were calculated according to equations (2) and (3).

Computational details

All calculations were performed within the framework of DFT as implemented in the Quantum ESPRESSO package [6]. For exchange-correlation energy, we employ a generalized gradient approximation using the Wu-Cohen (WC) parametrization [7]. A plane-wave energy cutoff was set to 50 Ry. For all calculations we used a 3×3×2 supercell of Ru, consisting of 36 atoms in the defect-free cell. In order to find the transition state and the migration energy barrier for the each saddle point structure the climbing image nudged elastic band method (CI-NEB) was applied [8]. The preliminary QHA calculation was provided using thermo_pw package [9] which utilize the density functional perturbation theory (DFPT) framework for phonon frequencies computing. Then vibrational properties for all energies required were obtained with the finite displacement method as realized in the Phonopy program package [10].

Results and discussion

The values of diffusion coefficients obtained for different temperatures were treated using a linear fit of $\ln(D)$ as a function of $1/T$ to obtain the effective prefactor D_0 and diffusion activation energy Q parameters of an Arrhenius plot

$$D = D_0 \exp\left(-Q / kT\right). \tag{4}$$

Fig. 1 shows the linear Arrhenius plots of vacancy-mediated Cu diffusion coefficients in hcp Ru within a basal plane and parallel (between adjacent basal planes) to the *c*-axis together with available experimental data [11]. One can see the diffusion rate within a basal plane is slightly higher than between adjacent basal planes in the high temperature range and becomes lower with decreasing temperature. In fact, diffusion of Cu in hcp Ru appears to be slower than in bulk TiN [12, 13] or TaN [14], which are currently used as diffusion barrier layers. Large deviation in the obtained values from available experimental data are probably explained by grain boundary diffusion, observed in this research, due to the polycrystalline nature of the Ru film.

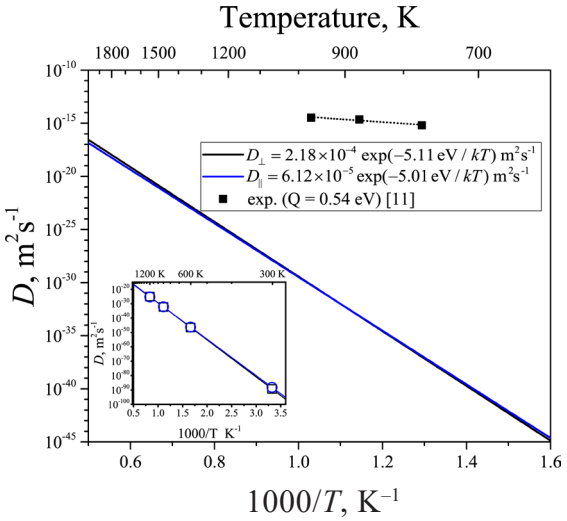

Fig. 1. Arrhenius plots of the calculated Cu diffusion coefficients in hcp Ru within a basal plane and between adjacent basal planes and experimental data corresponding to grain boundary diffusion [11]

Conclusion

We have performed a first-principles study of Cu impurity diffusion in hcp Ru. Arrhenius plots were obtained for vacancy-mediated diffusion within a basal plane and between adjacent basal planes. Our results confirm the excellent barrier properties of Ru against Cu diffusion, and the possibility of using Ru as a promising candidate to replace current state-of-the-art diffusion barrier technologies.

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THE AUTHORS

GOROKHOV Sergey A.
sgorohov@niime.ru
ORCID: 0009-0005-9636-3870

REZVANOV Askar A.
arezvanov@niime.ru
ORCID: 0000-0002-1677-9122

REZNIK Alexander A.
alreznik@niime.ru
ORCID: 0009-0004-3722-4865

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