J Mol Model (2007) 13:861–864
DOI 10.1007/s00894-007-0187-6

ORIGINAL PAPER

Interaction of copper organometallic precursors with barrier layers of Ti, Ta and W and their nitrides: a first-principles molecular dynamics study

Eduardo Machado · Marcin Kaczmarski · Benoît Braida · Pablo Ordejón · Diwakar Garg · John Norman · Hansong Cheng

Received: 8 January 2007 / Accepted: 9 February 2007 / Published online: 9 March 2007
© Springer-Verlag 2007

Abstract Processes for the deposition of copper films on transition metal barrier layers by means CVD using organometallic precursors are often found to lead to poor adhesion characteristics of the grown film. By means of first-principles molecular dynamics simulations, we show that the source of the problem is the strong reactivity of the surfaces toward the precursors, which decompose spontaneously upon contact with the surface leading to contamination of the interface. Our simulations consider Ti, Ta, and W as barrier layers, and Cu(hfac)-(tmvs) as precursor. In contrast, we show that surfaces of these metals properly passivated with nitrogen, in such a way that only N atoms are exposed on the surface, are much less active and do not lead to decomposition of the precursor. We propose this passivation procedure as a practical solution to the adhesion problem.

Keywords Chemical vapor deposition · Copper films · CupraSelect · Ab initio molecular dynamics

E. Machado · M. Kaczmarski · B. Braida · P. Ordejón
Institut de Ciència de Materials de Barcelona-CSIC,
E-08193 Bellaterra,
Barcelona, Spain

B. Braida
CNRS-Laboratoire de Chimie Theorique, tour 22–23,
Université Pierre et Marie Curie,
4 Place Jussieu,
75252 Paris Cedex 05, France

D. Garg · J. Norman · H. Cheng (✉)
Computational Modeling Center and Corporate Science
and Technology Center, Air Products and Chemicals, Inc.,
7201 Hamilton Boulevard,
Allentown, PA 18195-501, USA
e-mail: chengh@airproducts.com

The growing need of the microelectronics industry for metallization materials with improved properties has led to the search of alternatives to aluminum. Copper is an especially attractive metal for high-speed integrated circuits (IC), because of its low electrical resistivity and enhanced resistance to electromigration. However, copper, as well as other candidates for interconnects, shows a high diffusivity into the semiconductor, which must be avoided to preserve the proper operation of the device. The solution to this problem typically involves the growth of an intermediate layer of another metal with low diffusivity (so called "barrier layer") on the semiconductor before the deposition of the metallic film is done. Finding the most appropriate barrier layer is a problem that has attracted a great amount of activity, and an issue that is still not completely solved.

Chemical vapor deposition (CVD) is a very convenient method for deposition of metallic films on surfaces, due to the good quality (step coverage and via filling) of the films obtained and the scalability and ease of integration in the IC manufacture processes. Several organometallic compounds have been developed for this purpose. However, previous experience [1–4] has shown that copper films grown by CVD on diffusion barrier layers exhibit adhesion problems, which have been attributed to the presence of an amorphous layer containing fluorine, carbon and oxygen between the copper film and the barrier layer [5]. The formation of this layer is likely to be produced by the decomposition of the precursor upon contact with the surface.

In a recent publication [6], we studied by means of first-principles simulations, the interaction of one of the most common precursors for CVD deposition of copper layers, and of fragments of it, with Ta barrier layers. The precursor considered was Cu(hfac)(tmvs) [6], which can deposit pure copper films via a bimolecular disproportionation reaction

that produces a Cu (II) β-diketonate as a volatile byproduct [1]. We considered first the interaction of fragments of the Cu(hfac)(tmvs) compound, such as the •CF_3 radical, which was shown to decompose upon contact with the surface, leaving F and C species strongly chemisorbed on the surface. The same was found to happen with the complete Cu(hfac)(tmvs) molecule, which also decomposes on the surface yielding H, F and C atoms and other fragments of the precursor attached to the surface. These findings explain the existence of the amorphous layer observed in the experiments, which leads to poor adhesion.

In our previous paper, we demonstrated that a practical way to eliminate the problem of the surface contamination and to enhance the adhesion properties is to passivate the surface of the barrier layer, in such a way that the reactivity toward the precursor is reduced and decomposition is avoided. We proposed passivation of the Ta surface with N_2, to obtain a surface covered by TaN. If the passivation is complete, in such a way that the nitride surface only has N atoms exposed, our calculations showed that the resulting surfaces are no longer strongly reactive toward the precursor, which does not decompose upon contact with it. We proposed this as a practical way to avoid the chemisorption of chemical species from the precursor, and to eliminate the adhesion problems that are caused by them.

In this paper, we extend our previous studies on Ta surfaces to Ti and W as the metals for the barrier layer. We find that the bare metallic surfaces of Ti and W show high reactivity, similar to that of the Ta surface, and that the formation of nitrides also leads to passivation in these metals. Differences and similarities between the three metals considered will also be discussed.

We performed molecular dynamics (MD) simulations in which the energies and forces are obtained from first-principles, using the SIESTA method [7, 8], an implementation of density functional theory (DFT) [9, 10]. For details, we refer the reader to Ref. [6], where we describe the technical information that was also used in the DFT calculations presented in this work. For each system under considerations, several MD runs were performed, in which a Cu(hfac)(tmvs) molecule was thrown at the surface with a given initial velocity and orientation. The typical length of the MD runs was about 1 ps. Most of our runs were done at constant temperature, using the Nose thermostat technique [11], with temperatures ranging from 200 to 500 °C. We also did some simulations in the microcanonical (constant energy) ensemble, but we did not find any noticeable qualitative difference in the results obtained.

We first focus on the interaction of the Cu(hfac)(tmvs) precursor with the pure, clean metallic Ti, Ta, and W surfaces.

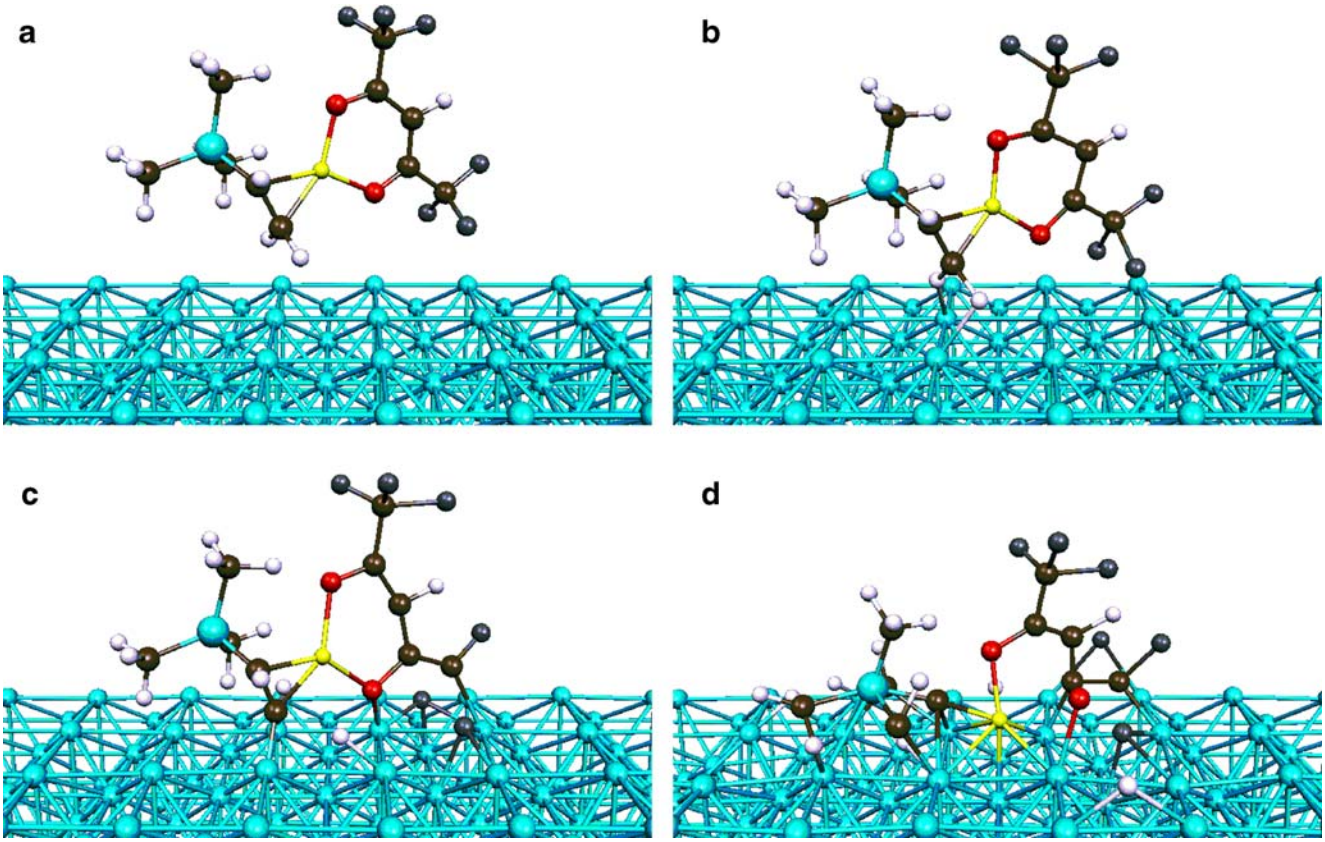

Fig. 1 Snapshots of four instantaneous configurations during a MD simulation of the interaction of Cu(hfac)(tmvs) with a W(001) surface

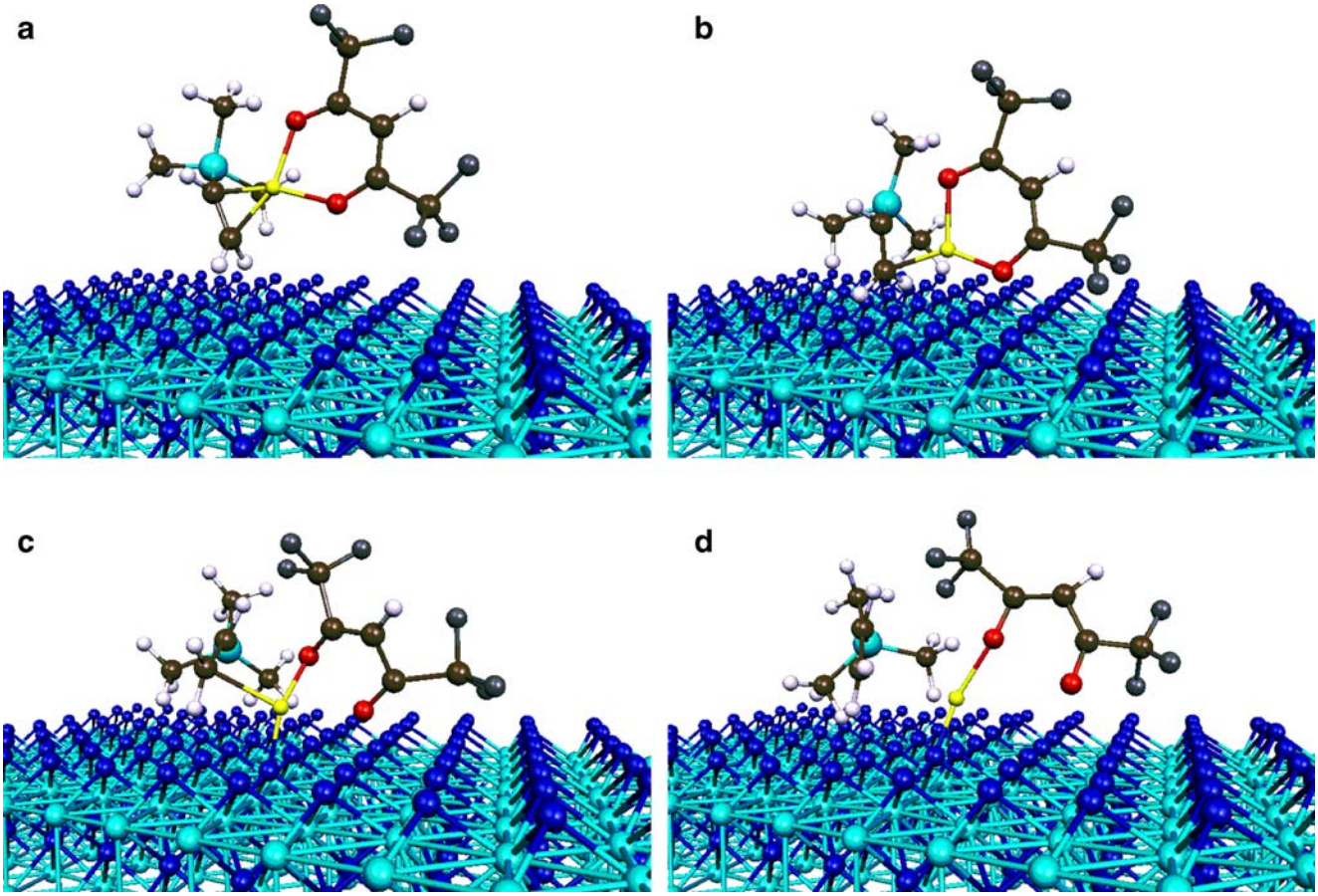

Fig. 2 Snapshots of four instantaneous configurations during a MD simulation of the interaction of Cu(hfac)(tmvs) with a hexagonal-WN (100) surface

In all our simulations, we systematically find that Cu(hfac)(tmvs) decomposes upon contact with the surfaces, quite independently of the initial orientation of the molecule with respect to the surface, its velocity and other technical parameters. As an example, Fig. 1 shows several snapshots of one of the MD runs for Cu(hfac)(tmvs) on the (001) surface of W. Also, in the other simulations not shown here, we see a similar decomposition as in the case of the Ta (001) surface reported in Ref. [6]. The chemical groups at the ligands break up upon contact with the surface, yielding H, C, O and F atoms attached on the top metal layer. In this particular run, the olefin group is the one that first collides with the surface and breaks up. Then, one of the CF_3 groups of (hfac) and two CH_3 groups of (tmvs) come in contact with the surface and decompose too. The Cu atom is released from one of the Cu-O bonds, and attaches to the surface. The corresponding O is also chemisorbed in atomic form, whereas the other O atom is still attached to the remaining fragment of the precursor for the duration of the simulation.

In all the simulations performed, we see that, even within the limited simulation time of a few picoseconds, the Cu(hfac)(tmvs) precursor clearly decomposes upon contact with the pure metal Ti, Ta, and W surfaces. The details of the final configurations depend on the initial conditions (orientation of the molecule with respect to the surface, direction of impact, initial velocity, temperature, etc). However, in all cases the surface ends up covered by a disordered ensamble of chemisorbed hydrogen, carbon, oxygen, and fluorine atoms.

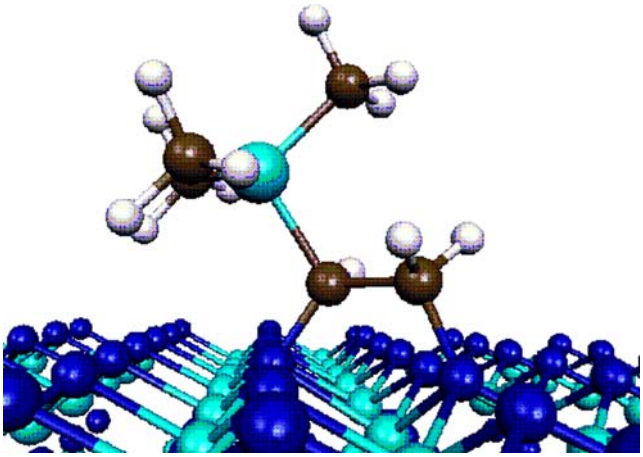

Fig. 3 Configuration of the olefin group of (tmvs) attached to the TiN surface

We now turn to the results for the N-passivated surfaces. We considered surfaces in which the termination is such that only N atoms are exposed, as in the TaN case we observed that the presence of metal atoms exposed on the surface still leads to high reactivity [6]. For TiN, we considered the (001) surface of the known cubic NaCl bulk phase [12]. For WN, we considered two possible crystalline structures reported in the literature: a hexagonal and a cubic NaCl phase [13, 14]. For these two phases, the surfaces fully covered by N are the (001) and the (111), respectively. However, our calculations show that the N- covered (111) surface of the cubic phase undergoes a strong relaxation of the first two surface layers, which shift with respect to the underlying planes, in such a way that the stacking order at the surface is changed into one very similar to that of the (001) surface of the hexagonal phase. Therefore, the atomic structure of the N-covered surfaces of both crystalline phases are very similar, which leads to very close properties of reactivity toward the Cu(hfac)(tmvs) precursor. Therefore, we will only show here results for the (001) surface of the hexagonal WN phase.

Figure 2 shows four snapshots of one of the simulations of the interaction of Cu(hfac)(tmvs) with the N-covered (001) surface of WN. As we observed for the case Ta [6], the N-passivated surface of W shows that the surface is selectively interacting with the precursor. The electron-rich surface N atoms repel the side groups of the ligands, avoiding the reaction and decomposition observed for the pure metal surface. During the simulation, we can observe that the Cu atom binds to the surface, while breaking its bond with the olefin group of (tmvs). For the remaining part of the simulation, the Cu atom remains bonded to the surface and to the (hfac) group. In all our simulations for WN, we observed similar trends, with no reactivity of the ligands with the surface.

For the case of TiN, the situation is similar in general: the precursor does not decompose upon contact with the surface, and Cu bonds to the surface layer. However, in some of our simulations we have observed some interaction of the olefin group of (tmvs) with the surface, as shown in Fig. 3. The binding energy of this group on the TiN surface is around 4 eV.

In summary, we have shown that the passivation of pure metallic Ti, Ta, and W surfaces by means of nitrogen strongly reduces the reactivity toward the Cu(hfac)(tmvs) precursor, and is a possible way to solve the adhesion problems of the Cu films observed on these surfaces. Whereas for Ta and W the passivation is complete, with no ligand groups being able to bind to the surface, for Ti we find that the olefin group of (tmvs) can bind to the N layer. However, even in this case, the ligands do not decompose on the surface.

Acknowledgements Work done under the auspices of the Simulations and Modeling Laboratory of MATGAS 2000 A.I.E. Some of the calculations were performed using the supercomputing facilities of CESCA, CEPBA, and CIRI. We acknowledge Air Products and Chemicals, Inc. for support of this collaborative research.

References

1. Norman AT, Muratore BA (1992) U. S. Patent No. 5,085,731
2. Cavallotti C, Gupta V, Sieber C, Jensen KF (2003) Phys Chem Chem Phys 5:2818–2827
3. Gandikota S, Voss S, Tao R, Duboust A, Cong D, Chen LY, Ramaswami S, Carl D (2000) Microelectron Eng 50:547–553
4. Voss S, Gandikota S, Chen L-Y, Tao R, Cong D, Duboust A, Yoshida N, Ramaswami S (2000) Microelectron Eng 50:501–508
5. Kröger R, Eizenberg M, Cong D, Yoshida N, Chen LY, Ramaswami S, Carl D (1999) J Electrochem Soc 146:3248–3254
6. Machado E, Kaczmarski M, Ordejon P, Garg D, Norman J, Cheng H (2005) Langmuir 21:7608–7614
7. Soler JM, Artacho E, Gale JD, Garcia A, Junquera J, Ordejón P, Sánchez-Portal D (2002) J Phys Condens Matter 14:2745
8. Ordejón P, Artacho E, Soler JM (1996) Phys Rev B 53:R10441–R10444
9. Hohenberg P, Kohn W (1964) Phys Rev 136:B864–B871
10. Kohn W, Sham LJ (1965) Phys Rev 140:A1133–A1138
11. Nosé S (1984) Mol Phys 52:255–268
12. Schöenberg N (1954) Acta Chem Scand 8:204–209
13. Schöenberg N (1954) Acta Chem Scand 8:213–220
14. Khitrova VI (1963) Kristallografiya 8:873–876