

Microstructural evolution and tribological behavior of Mo–Cu–N coatings as a function of Cu content

Jung Ho Shin^{a,b}, Qi Min Wang^{b,**}, Kwang Ho Kim^{a,b,*}

^a School of Materials Science and Engineering, Pusan National University, Busan 609-735, South Korea

^b National Core Research Center for Hybrid Materials Solution, Pusan National University, Busan 609-735, South Korea

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ABSTRACT

Ternary Mo–Cu–N coatings with various Cu contents were deposited on Si wafers and AISI 304 substrates by magnetron co-sputtering from two elemental targets of Mo and Cu in Ar–N₂ gas mixtures. The influence of copper content was investigated with regard to the microstructure, morphology, and tribological properties of these coatings. The results indicated that the Mo–Cu–N coatings exhibited face-centered-cubic B1–MoN phase structure. No diffraction peaks of Cu phase appeared in the coatings with Cu content below 11 at.%. The copper segregated in the amorphous inter-granular phase in the coatings. Incorporation of Cu into the growing Mo–N coating led to grain refinement. The average friction coefficient of the Mo–Cu–N coatings decreased from 0.40 to 0.21 with increasing Cu content up to 11 at.% due to formation of lubricious oxides of CuMoO₄.

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1. Introduction

Transitional metal (TM, such as Ti, Cr, and Mo) nitride coatings attracted much attention due to their high hardness, good mechanical properties, chemical inertness and high-temperature stability [1]. Among them, Mo–N coatings not only showed some unique physical and mechanical properties, especially high hardness and low solubility of nonferrous metals, but also exhibited a good adherence with steel substrates due to good solubility of molybdenum in iron based materials [2–5]. Besides, Mo–N coatings were reported to show low friction coefficients because of the formation of lubricious oxide of MoO₃ [5–7]. Therefore, Mo–N and their composite coatings are good candidates for wear resistant coatings in tribological applications.

By adding some soft metals (Cu, Ag) into the TM nitride (TiN, CrN, ZrN, MoN, etc.), a group of nanocomposite coatings with higher hardness and/or lower friction coefficient can be obtained, such as TiN–Cu [8], TiN–Ag [9], CrN–Cu [10–12], CrN–Ag [1,13], ZrN–Cu [14,15], Mo₂N–Ag [16,17], Mo–N/Cu [18]. Nanocomposite coatings present a unique opportunity to achieve better performance and durability in matching and manufacturing applications [19]. Among them, the Mo–N/Cu coating is a promising candidate for

wear-resistant use at elevated temperatures [20,21]. During tribological process, such as sliding and/or machining, oxides of both metals (Mo and Cu) are formed on the coating surfaces. MoO₃, a Magnéli phase, is an easy shearing oxide due to the weak bonding plane [20]. In addition, according to the “crystal-chemical model”, complex self-lubricating oxides from the binary alloy system with lower friction coefficient than that of the single oxides will form on the coating surface [22–25]. The properties of the self-lubricating oxide layer are related to the chemistry of the oxides. Öztürk et al. reported that the MoN–Cu and Mo₂N–Cu nanocomposite coatings exhibited lower friction coefficients and less wear rates against alumina counter-face as compared to the TiN–Cu and CrN–Cu nanocomposite coatings [18].

However, up to now, very limited studies on Mo–N/Cu films have been reported [18,26,27]. The detailed existence status of Cu in the Mo–N/Cu coatings was still not known. Appropriate coating design is important for the oxide-based lubricating coatings. More studies are needed to focus on the tribological properties of these coatings. It is important to investigate the strong tribo-chemical interactions between the coatings and the counterface materials.

In this study, Mo–Cu–N coatings deposited by magnetron co-sputtering from two elemental targets in Ar–N₂ gas mixture were explored. The effects of Cu incorporation on microstructure and tribological behavior of Mo–Cu–N coatings were systematically investigated.

2. Experimental details

2.1. Coating deposition

Ternary Mo–Cu–N coatings were deposited on Si (100) wafers and AISI 304 substrates using a magnetron co-sputtering equipment. A schematic diagram of the

* Corresponding author at: School of Materials Science and Engineering, Pusan National University, Busan 609-735, South Korea. Tel.: +82 51 510 3796; fax: +82 51 510 3360.

** Corresponding author. Tel.: +82 51 510 3796; fax: +82 51 510 3360.

E-mail addresses: qmwang@pusan.ac.kr (Q.M. Wang), kwhokim@pusan.ac.kr (K.H. Kim).

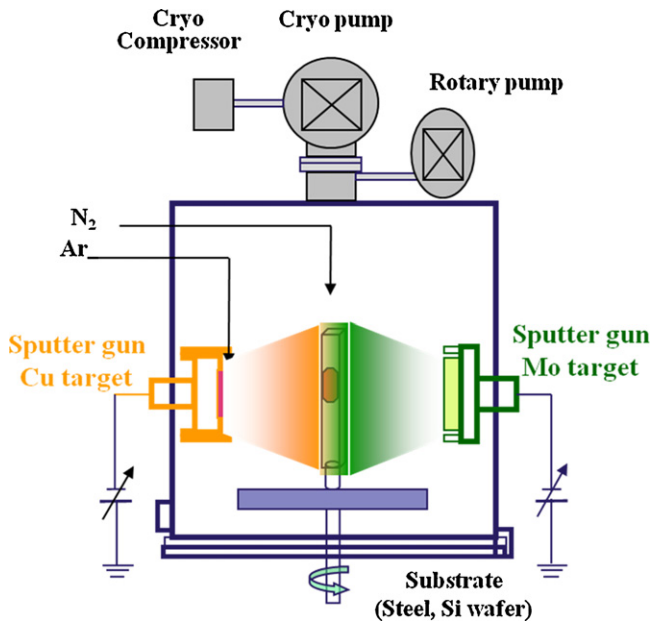


Fig. 1. Schematic diagram of a DC reactive sputtering system with separate targets for depositing Mo–Cu–N coatings.

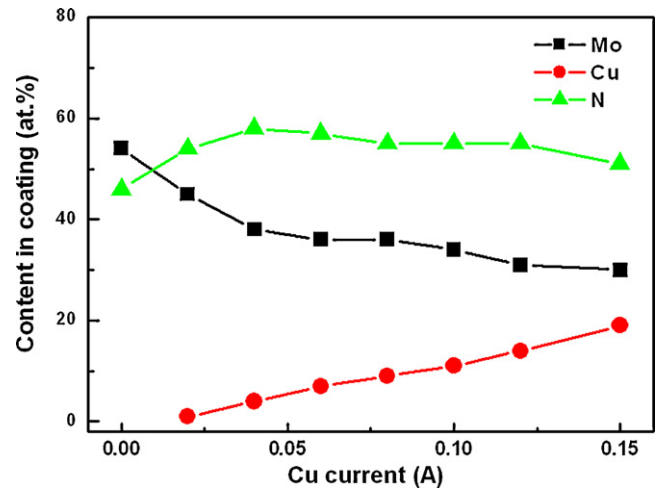


Fig. 2. Chemical compositions of Mo–Cu–N coatings (analyzed by EPMA) affected by DC sputtering current of Cu target.

apparatus is depicted in Fig. 1. The DC sputter sources of Mo (99.99%) and Cu (99.99%) were installed in opposite sides of the chamber wall. A rotational substrate holder was located on a straight line between the two sources, with distances from the two sputter sources to the substrate being 100 mm, respectively. The Si substrates with size of 20 mm × 30 mm × 0.7 mm were cleaned in an ultrasonic cleaner using acetone and alcohol for 30 min, respectively. The chamber was evacuated to less than 6.6×10^{-3} Pa and the substrates were heated to 180 °C. Mo–Cu–N coatings

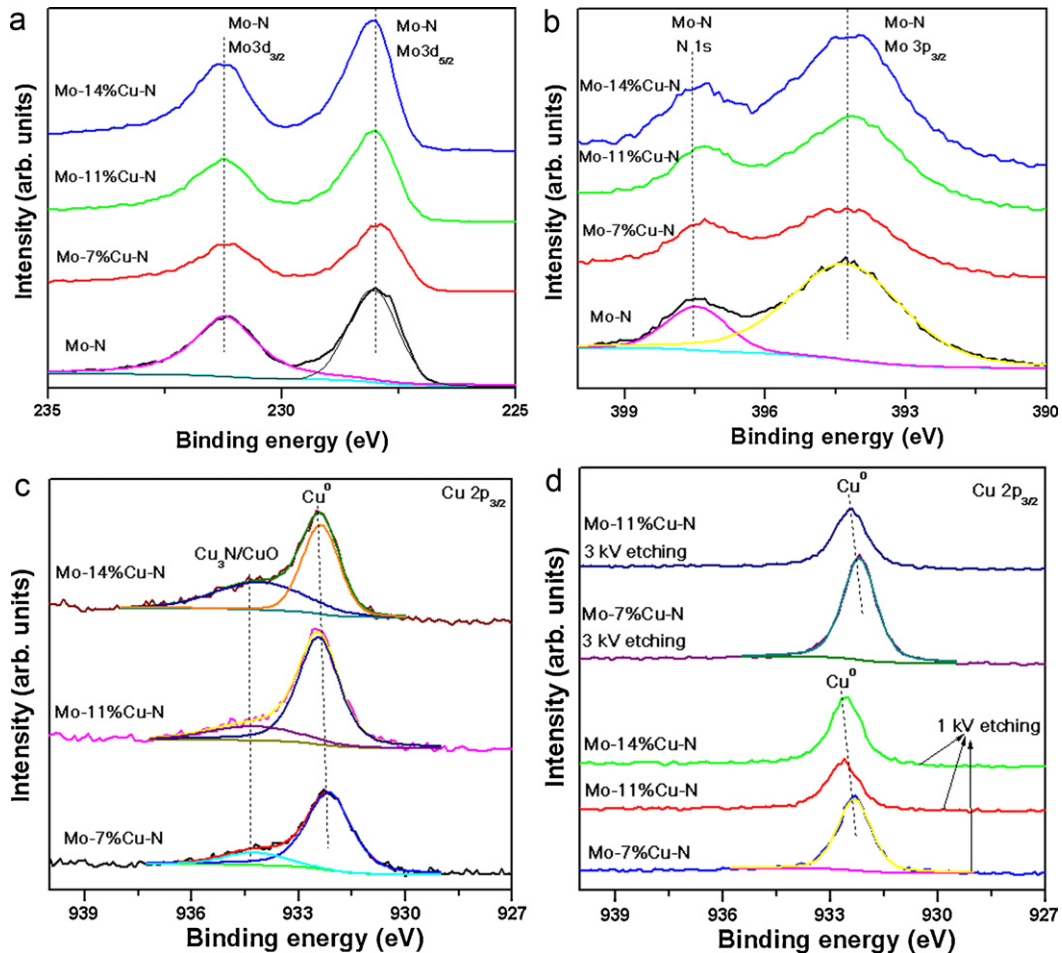


Fig. 3. Fitted XPS spectra of the various Mo–Cu–N coatings. (a) Mo 3d, 3 keV Ar⁺ ion sputtered surface; (b) N 1s and Mo 3p_{3/2}, 3 keV Ar⁺ ion sputtered surface; (c) Cu 2p_{3/2}, native surface; and (d) Cu 2p_{3/2}, coating surfaces after 1 keV and 3 keV Ar⁺ ion sputtering.

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