Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Materials Chemistry and Physics 95 (2006) 164–168
MATERIALS CHEMISTRY AND PHYSICS
www.elsevier.com/locate/matchemphys

Review

The rf-power dependences of the deposition rate, the hardness and the corrosion-resistance of the chromium nitride film deposited by using a dual ion beam sputtering system

Jongmin Lim, Chongmu Lee *

Department of Materials Science and Engineering, Inha University, 253 Yonghyeon-dong, lncheon 402-751, Republic of Korea

Received 9 July 2004; received in revised form 11 May 2005; accepted 17 May 2005

Abstract

The hexavalent chromium used in chromium plating is so toxic that it is very hazardous to human body and possibly causes cancer in humans. Therefore, it is indispensable to develop an alternative deposition technique. Dependences of the deposition rate, the phases, the hardness, the surface roughness and the corrosion-resistance of CrN_x deposited on the high speed steel substrate by using a dual ion beam sputtering system on the rf-power were investigated to see the feasibility of sputtering as an alternative technique for chromium plating. The dual ion beam sputtering system used in this study was designed in such a way as the primary argon ion beam and the secondary nitrogen ion beam are injected toward the target and the substrate, respectively so that the chromium atoms at the chromium target surface may not nearly react with nitrogen atoms. The hardness and the surface roughness were measured by a micro-Vicker's hardness tester and an atomic force microscope (AFM), respectively. X-ray diffraction analyses were performed to identify phases in the films.

The deposition rate of CrN_x depends more strongly upon the rf-power for argon ion beam than that for nitrogen ion beam. The hardness of the CrN_x film is highest when the volume percent of the Cr_2N phase in the film is highest. Amorphous films are obtained when the rf-power for nitrogen ion beam is much higher than that for argon ion beam. The CrN_x film deposited by using the sputtering technique under the optimal condition provides corrosion-resistance comparable to that of the electroplated chromium.

Keywords: Chromium nitride; Sputtering; Corrosion-resistance; Hardness; Deposition rate

Contents

1. Introduction

The chromium (Cr) plating technique has been widely used for decoration, corrosion-resistance, and wear-resistance in the field of automobile, electronic mechanical, chemical, paper, medical instrument industries since it was first commercialized in 1920. The hexavalent chromium used in chromium plating is so toxic that it is very hazardous to human body and possibly causes cancer in humans. A directive was declared that using hexavalent Cr, Pd, Cd and Hg be totally prohibited in fabricating automobiles which will be

* Corresponding author. Tel.: +82 32 860 7536; fax: +82 32 862 5546.
E-mail address: cmlee@inha.ac.kr (C. Lee).

0254-0584/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2005.05.039

sold since 2006. Therefore, it is urgently needed to develop an alternative technique with performance and cost competitive to the chromium plating technique. Many alternative deposition techniques including spray [1], ion plating [2], sputtering [3], ion implantation [4] and trivalent chromium plating [5] have been investigated for last several years. However, none of the alternative techniques seems to be satisfactory from viewpoints of performance and cost. Among the physical vapor deposition (PVD) techniques spray techniques such as thermal spray and plasma spray have been most widely investigated. Spray techniques are attractive since their deposition rates and process costs are high enough to compete with the electroplating technique. However, they are difficult to be used for depositing films on the surface of an objective with a complex geometry, for instance, the inside of a cylinder-shaped objective, because of its extremely narrow range of vision [6]. In comparison with the spray techniques, sputtering techniques offer much better step coverage, if only the specimen holder is designed to be rotated and tilted.

In fact the sputtering techniques have not been widely investigated as an alternative technique for electroplated chromium maybe because of their relatively low deposition rates compared with spray techniques, and thereby relatively high process costs particularly in reactive sputtering. The surface of a sputter target is often nitrified or oxidized during reactive sputtering in an atmosphere of nitrogen or oxygen, which is a main cause of reducing the deposition rate. Therefore, it is very important to separate the target and a substrate so that the reactive gas such as nitrogen and oxygen cannot get close to the target [7]. Several techniques developed for this purpose have been reported. These approaches include dual ion beam systems [8], sequential deposition and reaction [9], baffled magnetron [10], chemical cleaning of the target [11], and activation methods [12].

In this communication we report the deposition rate, the phases and the corrosion-resistance and the hardness of CrN_x deposited by using a dual ion beam sputtering system on the high speed steel substrate. This investigation was performed to see the feasibility of sputtering as a technique alternative to chromium plating. CrN_x was chosen as a hard coating material to replace Cr in this study since it has much higher hardness than Cr as well as almost the same corrosion-resistance as Cr. CrN_x thin films have a wide range of applications as protective coatings for cutting tools, die molds, and machine components owing to the merits such as high oxidation-resistance, high corrosion-resistance, high chemical stability, and low residual stress [13–15].

2. Experimental

A high speed steel which is used for making automobile parts and machine parts was used as a substrate material for CrN_x deposition. A flat high speed steel plate was cut into many small rectangular-shaped pieces with the size of 2 cm × 2 cm. The hardness and the rms-surface roughness of the substrate before film deposition was measured to be 820 Hv and 5.7 nm, respectively.

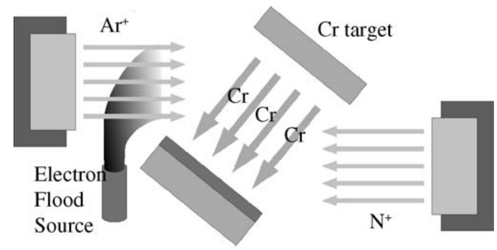

Fig. 1. A schematic illustration of the dual ion beam sputtering system.

CrN_x films with an approximate thickness of 3 μm were deposited by sputtering a Cr target in a dual ion beam sputtering system. A schematic of the dual ion beam sputtering system used in this study is shown in Fig. 1. It was designed in such a way as the primary argon ion beam and the secondary nitrogen ion beam are injected toward the target and the substrate, respectively so that the Cr atoms at the Cr target surface may not nearly react with nitrogen atoms. The distance between the target and the substrate was 10 cm. The rf-power for the primary and the secondary ion beam guns were varied in the range of 300–900 W. The nitrogen gas flow rate was varied in the range of 10–60 sccm. The substrate was heated to 200 °C and then kept constant at 200 °C by using a heating element of SiC. Alternatively room temperature was also used as a substrate temperature by using the cooling system since the substrate temperature due to the generation of plasma in the chamber was as high as 200–300 °C. The chamber pressure was kept at 50 mTorr by using the throttle valve near the inlet of the turbomolecular pump. The base vacuum was 3×10^{-6} Torr and argon and nitrogen gas flow rates were 20 and 15 sccm, respectively, during deposition.

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to measure the microstructures and the surface roughnesses of the CrN_x films. X-ray diffraction (XRD) analyses were performed to determine the degree of preferred orientation and to identify phases in the CrN_x films. The incident angle of the X-ray beam was 1.5° and Cu Kα characteristic X-ray was used in the XRD analyses. A micro-Vicker's hardness tester was used to measure the hardnesses of the CrN_x films. The hardness was measured by indenting for 20 s under the load of 1 gf. Also accelerated atmospheric corrosion tests were conducted in a salt spray cabinet (ASTM B 117-73) to investigate the corrosion-resistance of the CrN_x coatings. A 5% NaCl solution with a PH of 7.0 was used for atomization and the temperature of the spray cabinet was controlled to maintain 35 + 1.1 or −1.7 °C within the exposure zone of the closed cabinet.

3. Results and discussion

Deposition rate is one of the most important factors in developing a physical vapor deposition (PVD) technique