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Corrosion mechanism in PVD deposited nano-scale titanium nitride thin film with intercalated titanium for protecting the surface of silicon

Ali Usman Chaudhry¹, Bilal Mansoor¹, ^{2*} Tarang Mungole³, Georges Ayoub^{1,4}, David P. Field³

Abstract

In this work, thin film systems consisting of: (i) monolithic titanium nitride, (ii) monolithic titanium, and, (iii) titanium nitride with intercalated titanium, were fabricated on <100> P-type Si wafers by magnetron sputtering. The thin films were characterized using electron microscopy, glancing angle x-ray diffraction and nanoindentation. Their impedance response was studied via open circuit potential and electrochemical impedance spectroscopy in a sodium chloride aqueous solution. The influence of intercalated Ti thickness on impedance behavior was investigated in detail. Scanning electron microscopy analysis confirmed the columnar structure of TiN and aggregated structure of Ti thin films. Further microstructural analysis confirmed the presence of nano-porosities in thin films which explained their low modulus and hardness. Analysis of impedance data with equivalent circuit models indicated that incorporation of titanium as intercalated layer between titanium nitride and silicon surface, greatly altered the impedance characteristics of Si. Higher impedance values of thin films were achieved for bi-layer configuration at a much smaller total thickness as compared to monolithic counterparts. The increase in impedance was attributed to the presence of less defective and compact intercalated Ti layer that effectively interrupted the corrosive ions pathways.

Keywords: Silicon; PVD; thin films; corrosion; EIS; nanoindentation

1. Introduction

Thin films are known to improve the corrosion and wear resistance of various material surfaces used in several applications such as structural components [1], electronic materials and devices [2, 3], shape memory alloys [4], magnetic materials [5], and biomedical devices [6]. Currently, nano-scale ceramic-metal multi-layered thin films with promising mechanical, physical and chemical properties are of high interest for various extreme environment applications [7-9]. The ceramic overlay thin films of transition metal nitrides like titanium nitride (TiN) have very high thermodynamic stability and can be beneficial as protective coatings to improve the hardness, corrosion and wear resistance of a surface [10]. The major drawbacks associated with such coatings are presence of defects such as micropores and pinholes, which arise during deposition process [11]. Especially, physical vapor deposited TiN coatings have columnar microstructures and pronounced through-the-thickness pores in the structure. This structure impairs the mechanical and corrosion properties of such coatings. Moreover, these through-the-thickness defects allow corrosive media to reach the coating/substrate interface, resulting in corrosion of substrate and loss of coating adhesion [12, 13].

Various studies have showed that the corrosion resistance of the TiN coatings can be enhanced by increasing their packing factor, where packing factor of a thin film is defined as ratio of film density

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