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Microstructural properties of plasma-enhanced chemical vapor deposited WN_x films using WF_6–H_2–N_2 precursor system

Sam-Dong Kim *

Department of Electronic Engineering, Dongguk University, 3-26 Pildong, Joonggu, Seoul 100-715, Republic of Korea

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Abstract

A WF_6–H_2–N_2 precursor system was used for plasma-enhanced chemical vapor deposition (PECVD) of WN_x films. We examined the microstructural changes of the WN_x films depending on N_2/H_2 flow-rate ratio and post-annealing (600–800 °C for 1 h). As the N_2/H_2 flow rate was increased from 0 to 1.5, as-deposited WN_x films exhibited various different crystalline states, such as nanocrystalline and/or amorphous structure comprising W, WN, and W_2N phases, a fine W_2N granular structure embedded in an amorphous matrix, and a crystalline structure of β-W_2N phase. After post-annealing above 600 °C, crystalline recovery with phase separation to β-W_2N and α-W was observed from the WN_x films deposited at an optimized deposition condition (flow-rate ratio = 0.25). From this PECVD method, an excellent step coverage of ~90% was obtained from the WN_x films at a contact diameter of 0.4 μm and an aspect ratio of 3.5.

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Keywords: PECVD; WN_x; Thin film; Phase

1. Introduction

Great research effort has been made on tungsten nitride (WN_x) thin films because of their various promising applications for Si-based ultra-large-scale integrated-circuit (ULSI) devices, such as diffusion barriers for Cu interconnects [1–3], tungsten gate-electrode barriers controlling reaction between the tungsten and the gate dielectric [4], and high-dielectric-constant (ε_r) storage-node electrode barriers [5]. Diffusion barrier properties of the WN_x films depend on the crystalline phase; for example, W, W_2N and WN layers of 25 nm thickness were found to successfully prevent intermixing of Cu wiring with Si substrate after annealing at 650, 790 and 500 °C, respectively, for 30 min [1]. A variety of WN_x deposition methods have been reported thus far, such as sputtering [6,7], chemical vapor deposition (CVD) [8–10], and post-nitridation of tungsten films [11]. Compared to the sputtered WN_x films, the CVD films exhibit superior step coverage; therefore, they are more applicable to diffusion barriers for high-aspect-ratio structures, such as W-plug contacts, vias for damascene interconnects, and plug-type high-ε_r metal-oxide-metal capacitors.

As-sputtered WN_x films show an amorphous or a nanocrystalline structure and start to crystallize at temperatures ranging from 500 °C to 600 °C, depending on the film composition [2]. Effects of the process condition on the structural and chemical properties of reactively sputtered WN_x films were fully examined by Shen et al. [6]. From their work, an amorphous WN_x phase was produced in a composition range of 12–28 at.% nitrogen, whereas a single-phase structure of W_2N was shown at ~32 at.% nitrogen.

Low-pressure CVD (LPCVD) [9] or metallo-organic CVD (MOCVD) [10] can deposit both amorphous and crystalline films. However, the reported crystalline structures are quite different from one another because of their dissimilar process conditions. The plasma-enhanced CVD

* Tel.: +82 2 2260 3800; fax: +82 2 2260 8828.
E-mail address: samdong@dgu.edu

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(PECVD) WN_x deposition method, unlike the LPCVD or MOCVD methods, enables a low-temperature (400–500 °C) process, which is even compatible with the conventional Si interconnection processes. WN_x PECVD using a precursor system of WF_6–N_2–H_2 is especially interesting because it can process the films in a conventional tungsten CVD system by using the same reactor, thereby enabling *in situ* deposition of the WN_x diffusion barrier and the tungsten film without a vacuum break. However, microstructural and chemical properties of PECVD WN_x film depending on the process condition are not yet fully understood. In this article, results are presented for thin WN_x films produced by the PECVD method using a conventional W-CVD reactor with a WF_6–N_2–H_2 precursor system, and some new features not reported in previous CVD methods are revealed. We also examined effects of post-annealing on the evolutionary change in microstructure of the WN_x films by using various surface analyses.

2. Experimental procedure

All experiments used 8-inch p-type (1 0 0) Si wafers. The WN_x films were deposited in a tungsten-PECVD by using a WF_6–N_2–H_2 precursor system. Compared to the NH_3 in a WF_6–NH_3–H_2 or a WF_6–NH_3–SiH_4 gas combination, which is often used in thermal CVD methods, N_2 as a nitrogen source can give rise to a smaller deposition rate; however, it greatly reduces on-film particles due to the minimized gas-phase reaction. The number of on-wafer particles was measured in a particle counter before and after our WN_x film deposition, and the detected add-on particle counts were less than 30 per wafer. Deposition was performed in a CVD system at a heater temperature of 450 °C and a RF power of 200 W by varying the N_2/H_2 gas flow-rate ratio from 0 to 1.5. Flow-rate ratio was controlled by varying the flow rate of N_2 from 0 to 600 sccm under a constant H_2 flow rate of 400 sccm and a fixed chamber pressure of 1 torr. Prior to the WN_x film deposition, 1000-Å CVD SiO_2 layers were deposited to prevent any reaction between the Si substrates and the WN_x films during the depositions and/or post-annealings.

Optical reflectivities of the WN_x films were measured at i-line (365 nm) and were in good inversely proportional relationship with the atomic force microscopy (AFM) root mean square (RMS) values of film surface roughness. The AFM RMS values were measured by scanning an area of $5 \times 5\ \mu m^2$ on the specimens. Auger electron spectroscopy (AES) depth profiling and plane-view transmission electron

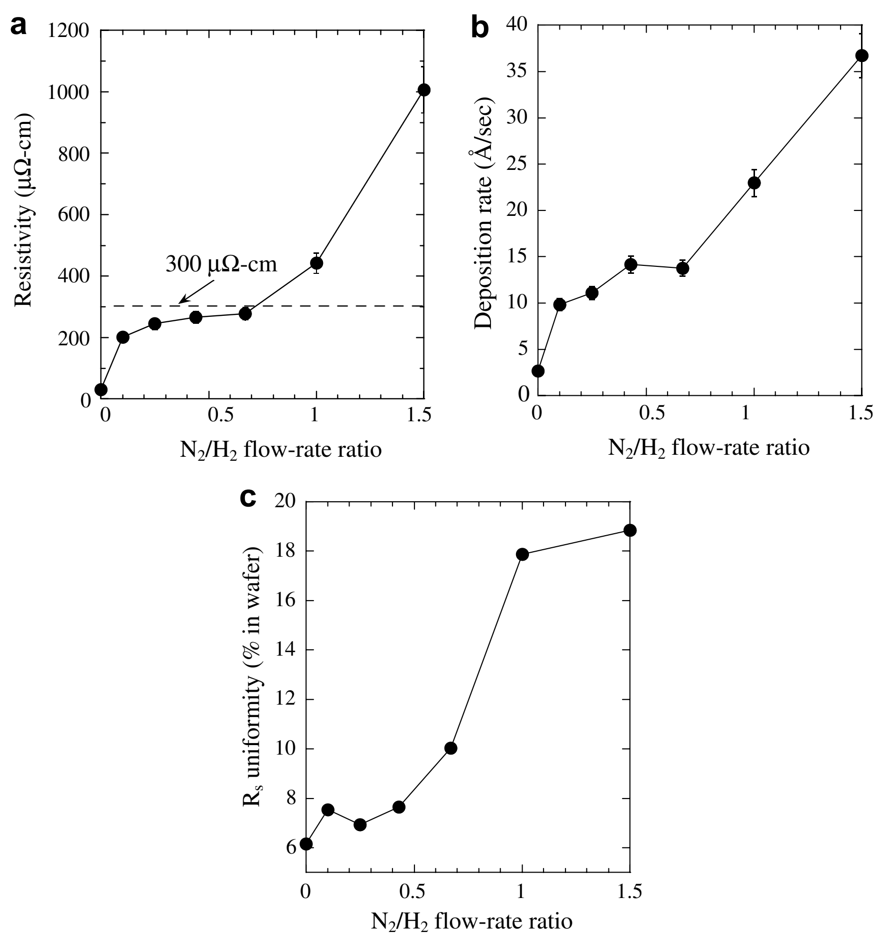

Fig. 1. (a) Electrical resistivity, (b) deposition rate, and (c) sheet resistance within-wafer uniformity of the PECVD WN_x films as a function of N_2/H_2 flow-rate ratio.