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Reactive pulsed laser deposition of thin molybdenum- and tungsten-nitride films

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Abstract

In this work reactive pulsed laser deposition of molybdenum- and tungsten-nitride thin films is investigated. Metallic targets were ablated in low-pressure (1, 10 and 100 Pa) nitrogen atmosphere by KrF excimer laser pulses (fluence ~6.5 J/cm^2). Films were deposited on silicon wafers heated to ~25, 250 and 500 °C. The characteristics of the films strongly depend on the N_2 pressure. By increasing N_2 pressure, the nitrogen content increases in the films, which leads to a monotonous increase of the electrical resistivity. Deposition rate decreases at 100 Pa as indicated by Rutherford backscattering spectrometry. At this pressure, hardness of the films significantly decreases also, as shown by microhardness measurements. X-ray diffractometry shows that films crystallinity is improved by increasing the substrate temperature. In addition, atomic force microscopy (AFM) and scanning electron microscopy (SEM) were applied for visualising the film surface.

Keywords: Laser ablation; Physical vapour deposition; Molybdenum nitride; Tungsten nitride

1. Introduction

Transition metal nitride thin films have many advantageous properties. These materials exhibit extreme hardness, high melting point, good chemical inertness and thermodynamic stability. Depending on the nitrogen content, their electrical resistivity can be tuned over a wide range [1]. Consequently, they are used as diffusion barriers and electrodes in semiconductor devices, as well as stable ohmic contacts for ultra large-scale integrated Si-technology [2] and as hard wear-resistant coatings [3]. Furthermore, they are well suited for several applications in the fields of engineering, machining, aeronautics, decoration as well as sensors [4]. TiN films have been extensively investigated by a number of deposition techniques [5–7]. Nitrides of refractory metals such as molybdenum and tungsten have attracted much less attention [8].

Pulsed laser deposition (PLD) is a powerful technique to deposit thin films, even from very hard materials. Moreover, reactive pulsed laser deposition (RPLD) is already established as a convenient technique for deposition of nitride films by ablating metal targets in a low-pressure nitrogen atmosphere [9]. In comparison with other techniques (e.g. vacuum evaporation or sputtering, which are also used to deposit W- and Mo-nitrides [8]), PLD is competitive with respect to deposition rate, chemical purity, adherence, and consistency of the deposited film. Recently, Soto et al. [10] have investigated tungsten nitride thin films deposited by reactive PLD technique from metal targets. They concluded that high quality and low resistivity dense tungsten nitride

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films can be fabricated by RPLD and that the atomic ratio x=[N]/[W] of the N in the WN_x films increases from x=0 to x=2 when increasing the N_2 pressure from 0 to 13.3 Pa.

The aim of the present study is to determine the optimal deposition conditions to produce high quality molybdenum- and tungsten-nitride thin films by reactive PLD in an efficient way. Molybdenum- and tungsten-nitride thin films were deposited from metallic targets in a nitrogen atmosphere on crystalline silicon substrates. The influence of the deposition temperature and reactive gas pressure was systematically studied from room temperature up to 500 °C and from 1 Pa up to 100 Pa, respectively. In addition, the processes that influence the film morphology and microstructure (i.e. target ablation, gas phase reactions, etc.) are discussed.

2. Experimental details

The experimental apparatus used for the deposition of our samples is described in detail elsewhere [11]. High purity (99.6%) Mo and W sheets (Goodfellow, 0.25 and 0.28 mm thick, respectively) were used as target materials. Substrates were cut from Si (100) wafers and cleaned ultrasonically in trichloroethylene, acetone, and isopropyl alcohol (10 min each) before they were introduced in the stainless steel vacuum chamber. The target-to-substrate distance in the reaction chamber was 4 and 3 cm for Mo and W, respectively. For each deposition, the reaction chamber was first evacuated to a pressure lower than 10^{-4} Pa, then it was filled up with N_2 (purity grade 6.0). Systematic series of experiments were performed at ambient nitrogen pressures of p=1, 10 and 100 Pa, while substrate temperatures were set to T=25, 250 and 500 °C at each pressure and for both materials. To ablate the metallic targets, focused KrF excimer laser pulses (λ=248 nm, average pulse energy ~200 mJ, pulse duration ~30 ns, repetition rate: 25 Hz) were used. The rotating Mo and W targets (0.2 Hz) were shot with 25,000 and 50,000 laser pulses, respectively. Average fluence at the target surface was ~6.5 J/cm^2. The incidence angle of the laser beam was ~45°.

The surface topography and particulate on the deposited films were examined by optical and scanning electron microscopy (SEM, secondary electron image mode). Atomic force microscopy (AFM) was applied for visualizing the fine structure of the film surface. The amplitude modulated dynamic (AC) mode AFM (MFP3D Atomic Force Microscope, ASYLUM Research, Santa Barbara, CA) was used for recording 2×2 μm scans. During the experiments conventional dynamic mode cantilever was used whose nominal spring constant was 5.5 N/m, and the resonant frequency was 170.3 kHz.

X-ray diffraction (XRD) investigations were performed at grazing angle (2°) using Cu-K_α radiation (λ=0.154 nm) of an INEL CPS 120 diffractometer equipped with a position sensitive detector and a computerized goniometer for grazing incidence analyses. The step size of the measured scans was 0.03° between 20° and 90°. The Scherrer method, applied to the Mo_2/N (111) and W_2/N (111) peaks, respectively, was used to estimate the mean grain size in the different samples.

The film thickness was determined from Rutherford backscattering spectrometry (RBS) measurements and computer simulations of the experimental data. The RBS spectra were recorded using 2.2 MeV He^+ ions, produced by a high voltage accelerator. To determine the electrical properties of the films, a four-point electrical conductivity probe was used. Finally, depth sensing indentation measurements were performed by using a Shimadzu DUH-202 type dynamic ultra micro hardness tester. Here, a Vickers pyramid was pressed into the surface of the samples at constant 6 mN/s loading rate up to 100 mN maximum load. After 1 s duration period, the indenter was pulled out from the material at the same rate. The hardness (H) was determined from the maximum load (P) and the remaining depth (d), using the formula H=38.584P/d^2. The units of P, d, and H were mN, μm and MPa, respectively.

3. Results

3.1. Surface morphology

Fig. 1a and b represent typical SEM images of the surface of a molybdenum- and tungsten-nitride layer, respectively. Most of the films have a smooth surface, without any cracks and waviness. Particulate can always be

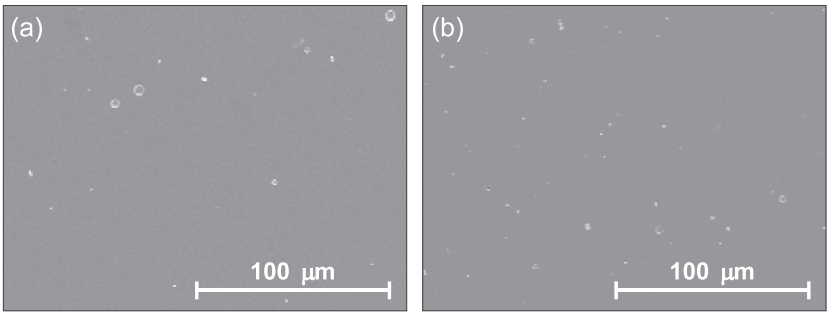

Fig. 1. SEM images showing MoN_x (a) and WN_x (b) film surfaces. Deposition parameters: T=25 °C and p=10 Pa.