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Nano-hardness estimation by means of Ar^+ ion etching

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ABSTRACT

When the coatings are in nano-scale, the mechanical properties cannot be easily estimated by means of the conventional methods due to: tip shape, instrument resolution, roughness, and substrate effect. In this paper, we proposed a semi-empirical method to evaluate the mechanical properties of thin films based on the sputtering rate induced by bombardment of Ar^+ ion. The Ar^+ ion bombardment was induced by ion gun implemented in Auger electron spectroscopy (AES). This procedure has been applied on a series of coatings with different structure (carbon films) and a series of coating with a different density (ZnO thin films). The coatings were deposited on Silicon substrates by RF sputtering plasma. The results show that, as predicted by Insepov et al., there is a correlation between hardness and sputtering rate. Using reference materials and a simple power law equation the estimation of the nano-hardness using an Ar^+ beam is possible.

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1. Introduction

A wide variety of wear and hardness test procedures have been developed such as: abrasion test scratch test, indentation and erosion test [1–3]. All methods are based on the evaluation of resistance of the materials to a certain type of mechanical damage. Nowadays the hardness estimation on material surfaces is based on nano-indentation [4]. In nano-indentation, a diamond tip is pressed with a specific load (the load range from mN to μN) on the surface of the material to leave a permanent deformation [5–7]. Following the load and un-load curve measured during the indentation process and applying the Oliver–Pharr method hardness and elastic modulus can be estimated [8]. Unfortunately, the measurements of mechanical properties of very thin film and in nano-materials are limited due to; dimension of indenter, instrumental resolution, influence of substrate and the surface roughness [9, 10]. Therefore, the development of a complementary mechanical test that can help the nano-indentation in estimation of the mechanical properties of materials in nano and meso scale is a crucial point [11]. In 2000 Insepov et al., proposed to use the cluster beam bombardment to measure the Brinell hardness of bulk materials [12,13]. They found a correlation between Brinell hardness available in literature and energy per sputtered atom (yield). Bringa and Johnson in 2002 compared the computational with experimental results and estimated the sputtering yield by parametrizing the crater volume in organic film [14,15]. Galleugher et al. in 2013 observed the difference of resistance to Ar^+ in ion milling between two phases of Zr-2.5 Nb. They correlated this behavior with the hardness. differences.[16]. Unfortunately in these papers the erosion rate, the real surface nano-hardness of material, and the effect of Ar^+ ion on nanostructured thin films were not reported. In this work, we focused on the evaluation of materials resistance towards the mechanical damage induced by an Ar^+ sputtering obtained by ion gun implement on Auger electron spectroscopy (AES) instrument. The Ar ion gun, in fact, can erode in control mode few atomic layers [17,18]. For that reason in this work, we consider the relationship between that mechanical properties and the sputtering rate. In the first part of the article, we study the mechanical properties of ZnO thin films with tailored density, focusing the attention on the correlation between hardness and sputtering rate of ion gun. In the second part we studied the sputtering rate and hardness in two carbon films, "hard" and "soft". Moreover, we merge hard-carbon and soft-carbon coating in different multilayer structures to obtain surface with tailored mechanical properties.

2. Experimental

2.1. Materials

The experiment has been applied on two different types of material: ZnO thin films and multilayer based on carbon film. ZnO thin films were deposited on 200 μm-thick n-type Si (100) substrates, at room temperature, by sputtering from a ZnO target in Ar/H_2 plasma discharges. Hydrogen concentration in the feed gas was varied from 0% up to 33%. The operative pressure and the cathode RF self bias were fixed at 50 mTorr and −550 V, respectively. The ZnO film thickness varied in the range of 769–300 nm. Two different types of carbon-based films were deposited, hard carbon film and soft carbon film. Hard carbon films (Hard-C) were sputter-deposited from a graphite target using an RF (13.56 MHz) plasma discharge. During the deposition process, the pressure was 0.05 Torr, and an Ar/H_2 mixture gas has been used [19].

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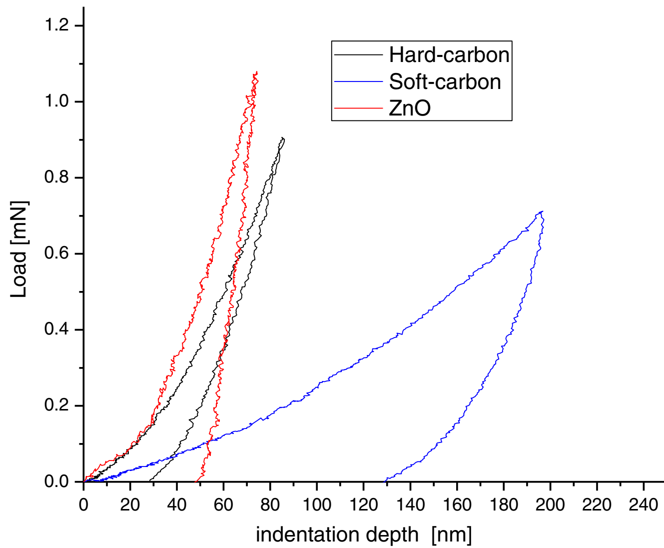

Fig. 1. Loading and unloading curve of ZnO, Hard C and Soft-C at ~1 mN.

The polymer-like carbon films (Soft-C) were obtained in $CH_4/H_2/N_2$ atmosphere using a plasma enhanced CVD (PECVD) process in a RF plasma discharge at 0.2 Torr. The two types of carbon film were combined in multilayer structures. The multilayer consists of alternating layers of soft polymer-like carbon films and hard amorphous carbon films. The total coatings thickness was kept almost steady (250 nm) while the number of layers was increased from 2 to 32 layers in a way that a single period thickness (Hard-C + Soft-C) varied from 14 to 125 nm, respectively. All coatings were grown at room temperature and floating potential on a 200 μm thickness n-type Si (100) substrate. The thickness was measured by using a stylus profilometer. The mechanical properties of the films were measured using depth sensing indentation by means of a CSM Nano-Hardness Tester instrument. The indentations were obtained with a Berkovich diamond indenter, applying the Oliver and Pharr model. The linear loading and unloading duration were kept as 30 s. All data reported in the present work are average values over ten measurements for each load. The experimental error was calculated as root mean square (RMS). In order to reduce the substrate effect, the indentations were performed within 10–20% of the total film thickness [19]. Auger electron spectroscopy (AES) is one of the most widely used analytical techniques for chemical analysis of the outermost material comprising a solid state surface. AES utilize a primary electron beam to excite the sample surface. Secondary electrons that are emitted as a result of a de-excitation process of a doubly ionized atom are analyzed and their kinetic energy is determined. Auger electron energy is characteristic of the element from which it was emitted. Qualitative and quantitative analyses of elements are achieved from the kinetic energy and the intensity of the Auger peaks, respectively. The nature of the Auger process is such that AES electrons can only escape from the outer (2–5 nm) of a solid surface at their characteristic energy. This effect makes AES an extremely surface sensitive technique. AES analysis provides detailed information on the elemental composition of materials and, when valence electrons are involved, on the chemical state of the surface atoms. All elements in the periodic table (except hydrogen and helium) are detected with moderate matrix effect. By combining Auger analysis with ion etching of the surface, a composition profile of elements as a function of depth may be achieved. AES depth profile raw data consist of peak-to-peak elemental signals as a function of the erosion time but a more commonly used in-depth composition plot is given by the elemental concentration as a function of the erosion depth. Therefore, a conversion of the measured erosion time into erosion depth and that of the peak-to-peak height to elemental concentration are required. Qualitative analysis is achieved using the elemental sensitivity factor method. In order to accurately investigate the distribution of elements into the film, an appropriate erosion rate has to be used. The velocity wherewith the surface is eroded can be described by an instantaneous erosion rate $\dot{z} = dz / dt$ which determines the mean eroded depth (z) as a function of the erosion time. A simple method to obtain the erosion rate ($\dot{z}$) is to measure the time required to erode through a layer of known thickness. Auger measurements were carried out using a PHI model 4200 Thin Film Analyzer instrument, equipped with a variable resolution cylindrical mirror analyzer (CMA, 0.3–1.2%) and a coaxial electron gun. The system base pressure was 1.0×10^{-9} Pa. The erosion

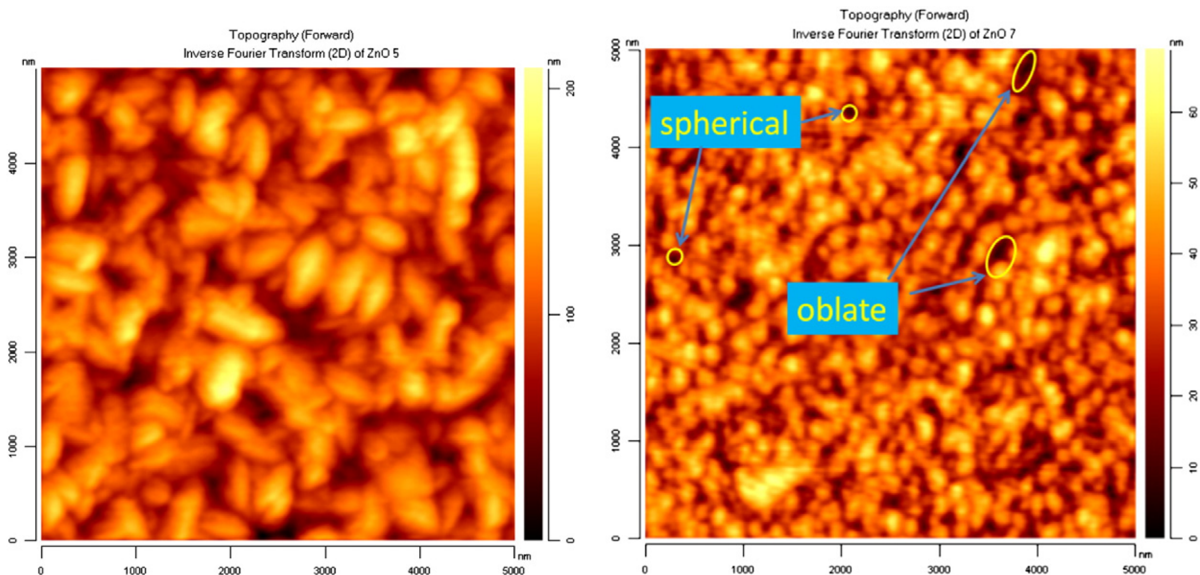

Fig. 2. AFM morphology of ZnO deposited in argon, porous in ZnO deposited in Ar–hydrogen plasma.

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