Synthesis of ZrN Film Via the Plasma Sputter-Type Negative Ion Source

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ABSTRACT

A plasma sputter-type negative ion source is used in the production of high grade coatings of zirconium mononitride (ZrN) on copper substrate. It presents a new approach for the production of ZrN thin films. The ion source was operated in its target/gas mode. Zirconium metal is used as target and argon as the sputtering gas. Nitrogen is used as the reactive gas. Optimum conditions for the synthesis of ZrN for a number of process parameters like volume ratio of gases, discharge conditions, substrate heating, bias, and deposition time were determined. Experimental runs using between 20% and 30% of nitrogen (with argon constituting the other 70-80%) in a total gas filling pressure of 7.0 x 10^{-3} Torr and an hour of deposition showed the synthesis of good samples by visual inspection in view of the typical gold color of the film produced. The target potential was between 300V to 325V and the target current between 7 mA to 12 mA. Discharge voltage was at 40V giving a plasma current between 698 mA to 1070 mA for the range of target potentials. The substrate was cooled to 20°C. The resulting layers were characterized by surface analysis methods like X-ray diffraction (XRD), atomic force microscopy (AFM), and energy dispersive X-ray analysis (EDAX). Films produced under these conditions exhibit the (100) and (200) peaks of ZrN obtained from the XRD analysis. The rms roughness from AFM were determined to range from 72 nm to 101 nm. Deposition rate was obtained at about 17 nm/min.

Key words: ion source, plasma, thin film, target, substrate

INTRODUCTION

Zirconium Nitride (ZrN) belongs to the three transition-metal nitride that includes titanium nitride and hafnium nitride having NaCl or A15 structure in general, with extreme stability in a generalized sense, that is, hardness, chemical inertness, and high melting point and Young's modulus (Ribbing & Ross, 1998). These films have been attracting much attention for various applications, such as Josephson junctions (Konuma & Matsumoto, 1977; Tanabe et al., 1987), diffusion barriers (Elbaum et al., 1983; Ostling et al., 1986; Igarashi et al., 1990), cryogenic thermometers (Yotsuya et al., 1987), hard coatings (Sproul, 1983), and others (Ribbing & Ross, 1998; Yoshitake et al., 1990) because of their high hardness and corrosion resistance, high thermal and chemical stability, and low resistivity *(13.6* mW-*cm)* (Jin & Maruno, 1991). ZrN films have been prepared on various substrates by several methods, including reactive sputtering (Tanabe et al., 1987; Elbaum et al., 1983; Ostling et al., 1986; Igarashi et al., 1990; Yotsuya et al., 1987; Sproul, 1983; Barnett et al., 1988; Jin, 1991), dual ion-beam sputtering (Johansson,

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1986), chemical vapor deposition (Karlsson, 1983), plasma arc (Konuma & Matsumoto, 1977), ion plating (Salmenoja, 1986), and others (Ribbing & Ross, 1998). The problem with the other deposition methods is the requirement of a high deposition temperature (< 500°C) for the effective formation of the ZrN films. Reference 18 lists the developments in this area worldwide.

In this research, the use of the plasma-sputter-type negative ion source *(PSNIS)* presents a new approach for the production of ZrN. This technique has some advantages over the conventional methods for ZrN film preparation. Substrate heating would not be necessary. And as in the case of TiN deposition, the flux and energy of the ions are controllable depending on the discharge conditions. Hence the chemical composition of the film can be controlled.

METHODOLOGY

A layout of the plasma production chamber facility is shown in Fig. 1. The Zr target is connected to a water-cooled copper electrode, which is biased negatively with respect to the plasma. The energy provided by the potential difference accelerates the positive argon ions across the plasma sheath and into the Zr target. The Zr ions are then produced and self-extracted into the diagnostic system.

A turbo molecular pump backed by a rotary pump evacuated the ion production chamber, and it normally attains a base pressure of 1.0 x 10^{-5} to 3.4 x 10^{-6} Torr.

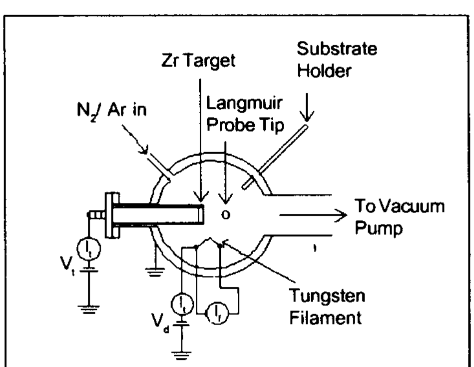

Fig. 1. Schematic Diagram of the PSNIS facility

The Ar/N_2 plasma was produced at an initial gas ratio of 20% and 30% N_2 in Argon with a total gas pressure of 7.0 x 10^{-3} Torr.

After the ignition of plasma, Langmuir probe traces were taken to determine the critical plasma parameters such as ion random current, plasma potential, and electron temperature. The samples were characterized using XRD for the crystal structure, SEM-EDS for surface morphology and elemental analysis, FIB for film thickness, and AFM for the roughness analysis of the films deposited on the substrate.

RESULTS AND DISCUSSIONS

Samples 1 and 2 have the following plasma parameters: deposition pressure of 7.0 x 10^{-3} Torr; filament current, 8.5 A; target voltage = –300 V; discharge voltage –40 V; chiller temperature, 20°C; and deposition time of 1.0 hr. Samples 1 and 2 have 30% N_2 and 20% N_2, respectively. Sample 1 will be referred to as 30% N_2 and sample 2 as 20% N_2. Tabulated data for the plasma parameters used in the experiment is shown in Table 1.

The x-ray diffraction patterns corresponding to the 30% N_2 (Fig. 2) and 20% N_2 (Fig. 3) confirms the presence of diffraction peaks as reported by Veszelei et al. and Horita et al.. The relative intensities of the peaks from this study show some variation from sample to sample, and do not necessarily match the random powder relative peak intensities from JCPDS file data for ZrN *(Card No. 02-0956)*. The reason for this is that there is a very likely preferred orientation of ZrN grains in the thin film compared to random orientation in the JCPDS powder specimens. The variation in relative intensities from sample to sample is not anomalous since such a variation can also be seen in the relative intensities of ZrN peaks from different investigators mentioned in reference (Veszelei, 1997; Horita et al., 1993).

Figs. 2 and 3 show the (111) and (200) peaks of deposited ZrN film on 30% N_2 and 20% N_2, respectively. The XRD machine was operated at 30 kV and 20 mA and with a divergence slit of 1/30 degrees with no receiving slit. Both samples show the (222) peak when the sample was operated at 20 kV and 15 mA with a

Substrate	1	2	I_T, mA	11.85	6.58
Base Pressure, Torr	1.0×10^{-5}	3.4×10^{-6}	V_D, V	- 40	- 40
P_{Ar}, Torr	4.9×10^{-3}	5.6×10^{-3}	I_D, mA	1070.1	698
P_{N2}, Torr	2.1×10^{-3}	1.4×10^{-3}	V_S, V	-	- 40
$P_T = P_{Ar} + P_{N2}$	7.0×10^{-3}	7.0×10^{-3}	T_C, °C	20	20
% N_2	30	20	t_d, hrs	1.0	1.0
% Ar	70	80			
I_F, Amp	8.5	8.5	Film thickness, nm	1030	1055
V_T, V	- 300	- 300	Deposition rate, nm/min	17.17	17.60

Table 1. Plasma parameters used during the experimental runs ***(on Cu substrate)***

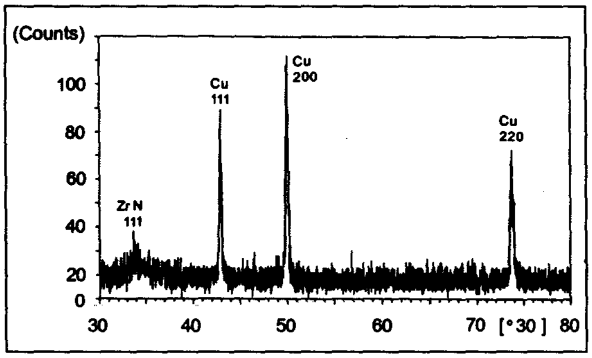

Fig. 2. XRD pattern of 30% N_2 showing the (111) ZrN peak

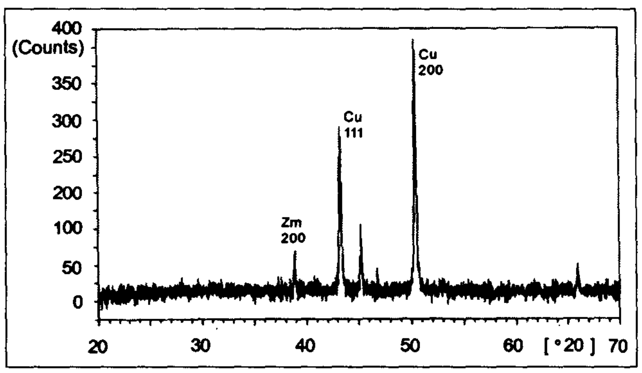

Fig. 3. XRD pattern of 20% N_2 showing the (200) ZrN peak

divergence slit of 1 degree and a receiving slit of 0.1 degrees at different sample orientation.

The evidence of the presence of elements composing the film is shown in Figs. 4 and 5 obtained by EDS characterization. The Cu peak is attributed to the substrate.

The surface roughness of the deposited film was determined by AFM. It is important since it can influence electronic transport. There are many ways of measuring surface roughness, but among the most useful measures are the mean roughness and the rms roughness. The rms roughness is usually preferred over the mean roughness since it involves the sum of the squares of the deviation from the fitted plane surface, which is always positive quantity. 30% N_2 has a mean roughness of 57.663 nm and rms of 71.914 nm as shown in fig. 6 .20% N_2 has a mean roughness of 79.148 nm and rms of 101.44 nm, fig. 7.

Thus, 30% N_2 had (111) and (222) XRD peaks shown in Fig. 2 with film thickness of 1030 nm and deposition rate of 17.17 nm/min. 20% N_2 had (200) and (222) XRD peaks as shown in Fig. 3, with film thickness of 1055 nm and deposition rate of 17.60 nm/min. Langmuir Probe traces were used for the calculation of ion random current, electron temperature, and plasma potential.

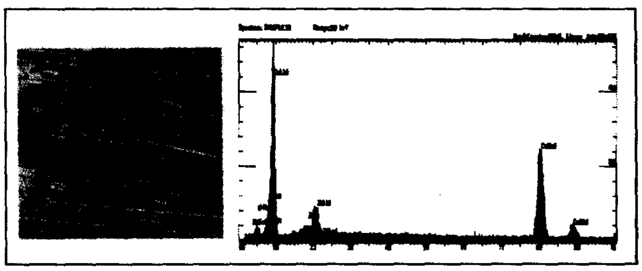

Fig. 4. SEM image and EDS Spectra of 30% N_2

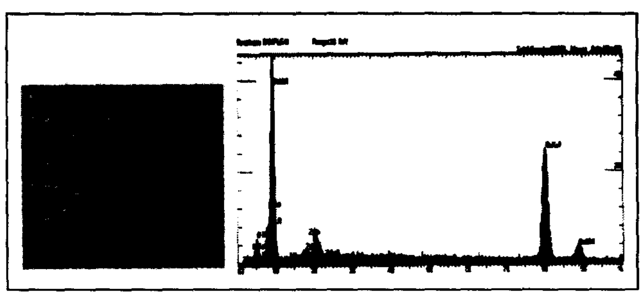

Fig. 5. SEM image and EDS Spectra of 20% N_2

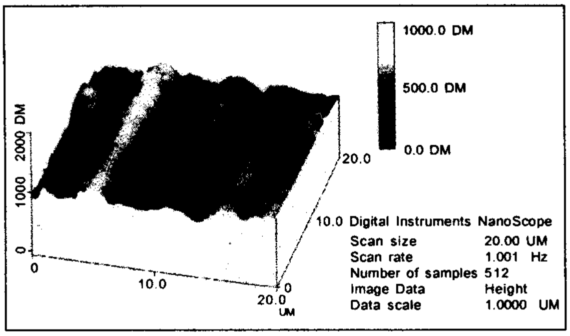

Fig. 6. AFM 3D image of 30% N_2

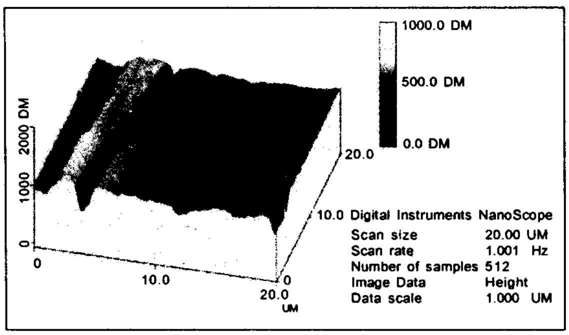

Fig. 7. AFM 3D image of 20% N_2

For 30 % N_2, the results were as follows: ion random current, -0.1257 A; electron temperature, 3.50 X 10^4K; and plasma potential, 10.37 V. The results for 20 % N_2 were: ion random current, -0.1113 A; electron temperature, 3.32 X 10^4K; and plasma potential, 10.49 V.

The objective of the research, which is to grow a ZrN film on Cu substrate, was realized under a different nitrogen pressure condition. Further study on the correlation of the plasma parameters and Langmuir Probe traces with the film grown on the substrate is still on-going.

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