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Investigation of reactive HiPIMS + MF sputtering of TiO_2 crystalline thin films

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ABSTRACT

A hybrid high-power impulse magnetron sputtering (HiPIMS) + mid-frequency (MF) magnetron sputtering system was used for the deposition of crystalline TiO_2 thin films at a low substrate temperature. Ion velocity distribution functions (IVDFs) were measured in a pulsed magnetron discharge at substrate positions depending on the type of plasma excitation and on the working gas mixtures. Several different pulsed discharge configurations were used: (i) HiPIMS, (ii) pulsed bipolar MF with frequency 350 kHz and (iii) both HiPIMS + MF connected in parallel to the magnetron cathode. The timing of HiPIMS excitation was set to period time $T = 10$ ms with "ON" time $T_{ON} = 100$ μs. Ti targets were sputtered in three different types of atmospheres: (i) inert pure Ar, (ii) a reactive mixture of Ar + O_2 and (iii) a reactive mixture of Ar + O_2 + N_2 with a constant gas pressure $p = 1$ Pa. All IVDFs were measured using a time-resolved retarding field energy analyzer (RFEA) located in the substrate position. TiO_2 thin films were deposited under identical experimental conditions on silica (SiO_2) glass substrate, glass with an indium tin oxide (ITO) electrode and polycarbonate polymer foil. The thin film properties are discussed with respect to the measured plasma parameters. It is shown that the combination of HiPIMS + MF excitation in a reactive atmosphere effectively reduces the delay between the edge of cathode voltage and current onset. The highest ion energy was reached in the case of an inert Ar atmosphere due to the highest ratio of fast Ti^+ ions in the overall ion flux. All TiO_2 thin films deposited in reactive atmospheres formed pure rutile phase regardless of the excitation mode; however, those films deposited by a HiPIMS + MF excitation mode exhibited the greatest ability to produce a photocurrent. Furthermore, HiPIMS + MF was the best setting for the deposition of crystalline TiO_2 on polycarbonate foil because of the low heating flux on the substrate and suitable plasma parameters leading to the formation of the rutile phase.

1. Introduction

Magnetron sputtering (MS) is a widely used physical vapor deposition (PVD) technology that is used to grow many types of thin films on various substrate materials. Pulsed excitation of magnetron sputtering allows both the reduction of the substrate temperature during deposition and a considerable increase in the plasma density in the pulse-on time at a constant average discharge power [1]. The increase in the plasma density promotes formation of a denser and more stable film structure that leads to the improvement of the film properties [2,3]. High-power impulse magnetron sputtering (HiPIMS) technology is differentiated from other types of magnetron sputtering by its extremely high degree of ionization of the sputtered material achieved by applying high peak powers (~kW/cm^2) during short duty cycles (<10%) [4,5]. A typical HiPIMS discharge operates at a pulsing frequency of 50–1000 Hz, with the peak current density at around 4 A/cm^2 [6]. Under these conditions, the plasma density near the target increases enough to ionize a significant proportion of the sputtered metal ions [7,8]. The energy of these impinging metal ions can be tuned using the external substrate bias to improve thin film adhesion, density or texture [9]. Moreover, under certain HiPIMS discharge conditions, the total energy flux density to the substrate is lower than that of a conventional DC magnetron sputtering under the same average discharge power [10].

HiPIMS magnetron systems have been previously studied in combination with mid-frequency (MF) plasma excitation [11,12]. Some advantages of these systems stem from the possibility of utilizing the "OFF" time of the duty cycle, thereby enhancing the deposition rate, decreasing the working pressure, and improving HiPIMS plasma generation as a result of MF plasma pre-ionization.

Many papers dealing with the characterization and measurement of some basic parameters of HiPIMS plasma have been published [4,13–18]. There is a marginal interest in the scientific community in the dependence of thin film properties on the parameters of HiPIMS plasma and in a comparison of plasma parameters in various excitation modes. It was shown that some of the most important parameters, with fundamental influences on the quality of deposited layers, are the energy of impinging ions, the density of charged particles and the degree of ionization of sputtered particles [19]. The deposition rate is usually lower in HiPIMS mode, even when compared with that of a classical DC magnetron. Some exceptions to this rule may be found for example in [20–22], where the deposition rate

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achieved was almost 120% of the dcMS value. The concentration of charged particles in HiPIMS mode, however, is higher by as much as an order of magnitude.

In the present study, a retarding field energy analyzer (RFEA) was used to measure the time-resolved ion velocity distribution function (IVDF) in a high-power pulse plasma under various modes of excitation. Pure HiPIMS, medium-frequency pulsed bipolar (MF — 350 kHz) and hybrid pulsed HiPIMS + MF low-pressure magnetron sputtering were investigated and the IVDF in inert (Ar) and in a reactive (Ar + O_2, Ar + O_2 + N_2) atmosphere of high power pulsed plasma within the short duty cycle of the period was characterized. The resulting data are then correlated with the properties of deposited TiO_2 layers.

2. Experimental setup

2.1. Experimental setup of deposition system

The scheme of the experimental setup is shown in Fig. 1. The UHV reactor was continuously pumped by a turbo-molecular pump backed by a combination of roots and rotary vane pumps. After achieving a base pressure of less than 10^{-5} Pa, the chamber was backfilled with a working gas (Ar, Ar + O_2 or Ar + O_2 + N_2) to an operating pressure 1 Pa. During the deposition, the flow rates of Ar, O_2 and N_2 gases were fixed at 15 sccm each. The Lesker TORUS magnetron was equipped with a titanium target 5 cm in diameter with a typical purity of 99.7% and used a sputter down magnetron arrangement.

The magnetron was operated in several modes: (i) high power impulse magnetron sputtering, (ii) mid-frequency pulsed bipolar magnetron sputtering (MF — 350 kHz) and (iii) a combination of both hybrid DC pulsed HiPIMS + MF. The HiPIMS power supply unit was capable of drawing up to a maximum peak current of 200 A in a pulse and a maximum average current of 10 A. A ballast resistor of 5.5 Ω that was incorporated into the power switch unit stabilized the pulse discharge current. The repetition frequency of HiPIMS pulses was held at 100 Hz ($T = 10$ ms), and the active plasma pulse time was set to 100 μs (duty cycle 1%) for all experiments. The time-averaged discharge current was 500 mA, and the average absorbed HiPIMS power was 200 W. Under these conditions, the peak discharge current could reach a value

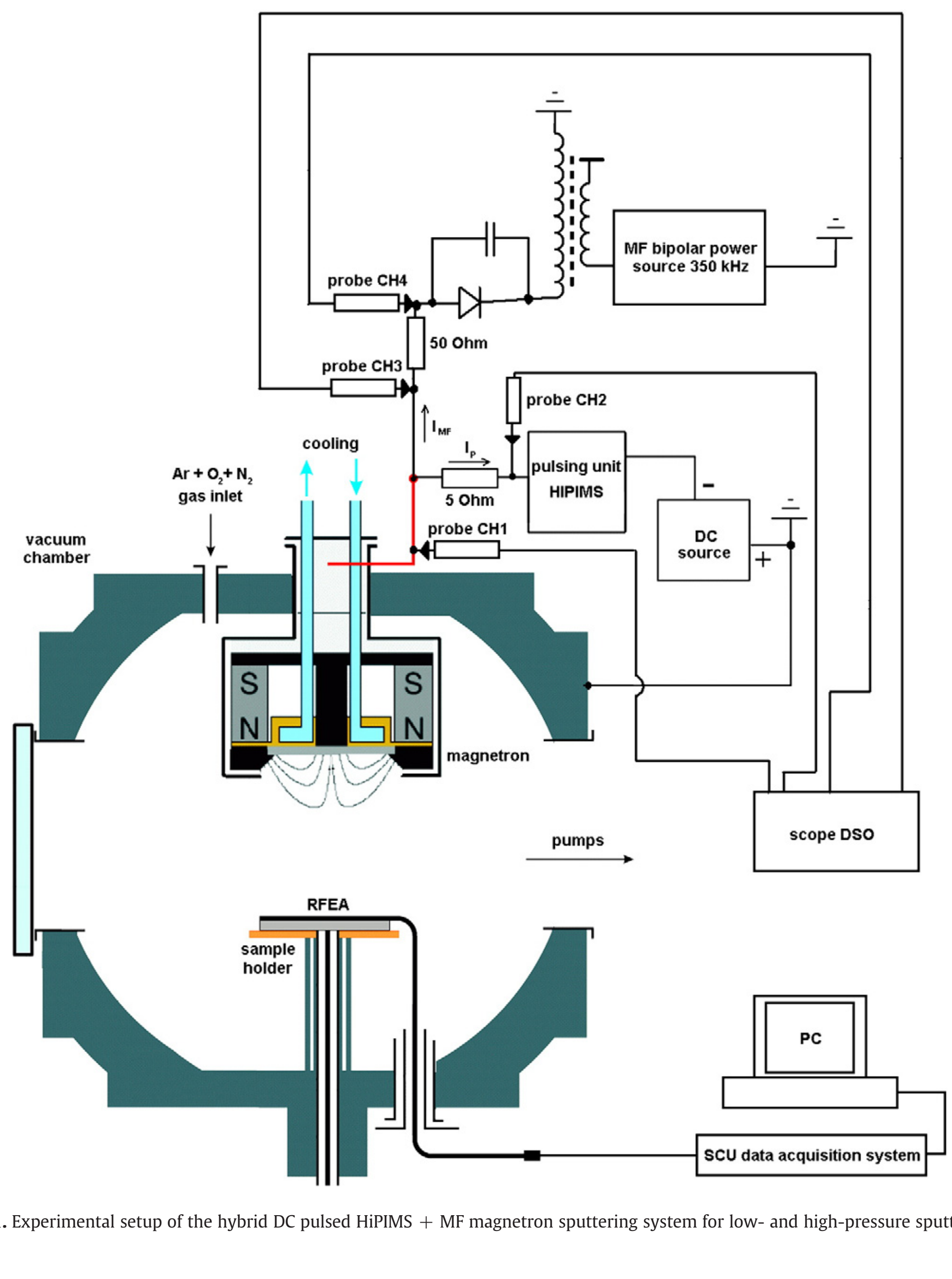

Fig. 1. Experimental setup of the hybrid DC pulsed HiPIMS + MF magnetron sputtering system for low- and high-pressure sputtering.