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Synthesis and characterization of plasma assisted chemically vapor deposited tantalum

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ABSTRACT

This study focuses on the synthesis of tantalum (Ta) coatings on high strength steel by plasma assisted chemical vapor deposition using tantalum pentachloride ($TaCl_5$) as a preferred precursor and hydrogen (H_2) as a reducing agent. The interrelationships governing the growth kinetics, compositions, and coating properties are discussed as a function of deposition temperature, total pressure, and gas composition. The synthesized tantalum coatings are shown to be essentially pure with trace amounts of oxygen, carbon, and chlorine. The coatings are found to be dense and to exhibit conformal coverage. Preferential formation of the α-Ta phase is noted to occur when coatings are grown sequentially and in-situ on a TaN_x seed layer.

1. Introduction

The use of tantalum (Ta) as a protective coating for the interior bore surfaces of gun barrels is of current interest [1–5]. The motivation for this choice of material arises from the need to replace chromium (Cr) coatings which are electro-deposited from aqueous solutions of hexavalent chromium, a known carcinogen and toxic substance that is strictly regulated and entails high disposal costs [6]. In the past, Cr has proven to be quite effective due to its chemical inertness as well as its excellent adherence and close thermal match to the substrate. However, current lethality requirements have increased to the point where Cr has become thermally overmatched and the resulting wear life has declined to unacceptable levels. Furthermore, the cracking tendency of Cr remains a serious issue that is incompatible with the ever-increasing need for higher muzzle energies (~20 MJ) and hotter propellants (~3673 K). Cr cracking provides a path for the hot propellant gases to reach the lower melting substrate, resulting in a lift-off of the coating and subsequent exposure of the underlying steel to excessive wear and erosion [7]. In comparison to Cr, Ta offers advantages that include a higher melting point (3290 vs. 2148 K) and higher ductility (α-Ta) that leads to better resistance to thermal shock and cracking and, thus, higher resistance to corrosive propellant by-products attack of the substrate [8,9].

Although internally magnetized cylindrical magnetron sputtering (IM-CMS) is an acceptable deposition method for cylinders with internal diameters of 60 mm and greater, it has proven not to perform well on cylinders with diameters below 45 mm since the smaller bore diameter of medium caliber guns cannot accommodate the critical ionization distance required for this process [10]. Generally, sputtering is a room temperature process that limits inter-diffusion at the substrate–coating interface. This creates adhesion difficulties, which in turn leads to more extensive surface preparation (cleaning). Another important consideration particularly pertinent to medium caliber guns, where the bores are rifled as compared to being smooth for large caliber guns, is that sputtering is a "line-of-sight" technique, thus, limiting the uniform coverage required for proper wear and erosion protection along spiraled paths.

Chemical vapor deposition (CVD) offers promising solutions to the problems associated with IM-CMS coatings. It is a well-established technique that offers the capability for relatively low temperature processing (e.g. by using plasma), thus, denying the underlying substrate from experiencing process induced crystallographic changes or damage, and contamination by diffusion of impurities [11]. Reported studies have also indicated that high quality CVD tantalum coatings can be produced at deposition temperatures in the range of 523 to 723 K with excellent step coverage in sub-micron trench structures with high aspect ratios [12,13]. This study explores the use of plasma assisted chemical vapor deposition (PACVD) to produce Ta coatings on high strength steel substrates at relatively low temperatures. The Ta coatings synthesized in this study, under various processing conditions, were characterized with respect to their chemical, structural, and morphological properties in order to ascertain the quality of the deposits.

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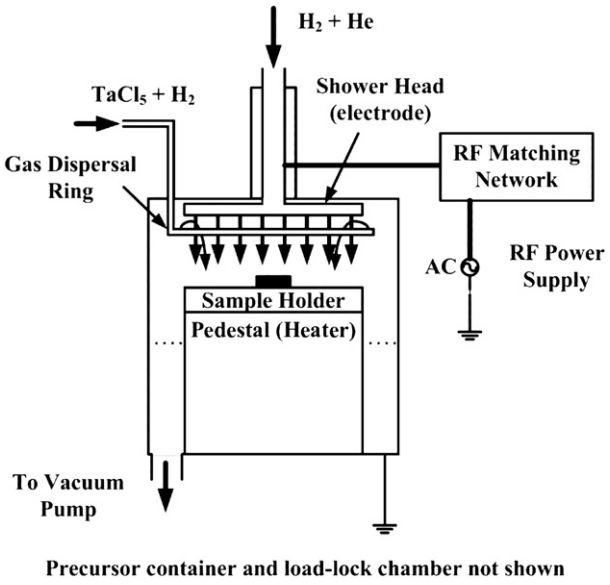

Fig. 1. Schematic diagram of PACVD reactor.

2. Experimental details

Fig. 1 illustrates the schematic diagram of the homemade single wafer "warm" wall PACVD reactor used in our experiments which allowed for processing substrates up to 150 mm in diameter. The reactor was connected to an Edwards QDP 80 vacuum station comprised of a mechanical pump and roots blower that operated at a base pressure of 0.71 Pa. The pressure in the reactor was measured at the reactor inlet using a vacuum gauge with a 0–1.3×10^3 Pa range and controlled by a throttle valve pressure controller to maintain constant pressure. An Advanced Energy RFX-600 with a frequency of 13.56 MHz was used as the source of radio frequency (RF) power and was connected to an RF matching network for impedance matching. The reactor was equipped with a load lock to prevent atmospheric contamination on the surface of samples. The load lock was isolated from the reactor by a pneumatically operated slit valve and evacuated using a rotary pump. Sample transfer was achieved through a manual load lock arm.

The use of tantalum halide precursors such as TaF_5, $TaCl_5$, and $TaBr_5$ has been reported in the synthesis of CVD Ta coatings [13,14]. The heat of formation of these precursors is found to increase in the following order: $TaBr_5$ (−598 kJ/mol)<$TaCl_5$ (−858 kJ/mol)<TaF_5 (-1.90×10^3 kJ/mol) [15]. At a given temperature, the vapor pressure of these halides consequently follows a reverse order (at 393 K): $TaBr_5$ (~2.67 Pa)<$TaCl_5$ (~400 Pa)<TaF_5 ($\sim1.33\times10^4$ Pa) [15,16]. Based on this data, $TaCl_5$ was selected because of its mid-range optimal values. In this experiment, $TaCl_5$ with the purity of 99.99% is used, which is supplied by Cerac, Inc. (Milwaukee, Wisconsin, USA). It is a solid powder form with nominal particle size of less than 4.75 mm. The overall chemical reaction occurring using tantalum chloride is as follows:

$$2TaCl_5(g) + 5H_2(g)\ 2Ta(s) + 10HCl(g)$$

Mass flow controllers were used to measure and control the flow rate of all process gases. H_2 was used as a reducing agent and He gas was added to enhance excitation or ionization of the precursor [17]. Both gases were delivered through a shower head located above the substrate. The shower head also served as the powered RF electrode. The $TaCl_5$ precursor with H_2 carrier gas was delivered through a gas dispersal ring (Fig. 1). The cooling ring was attached with the gas dispersal ring to prevent the decomposition of the precursor inside the ring. N_2 was used as a coolant. The precursor was contained in a stainless steel bubbler. The precursor bubbler and delivery line were heated and controlled by a Watlow anafaze CLS 208 heat controller. The temperature of the delivery line was set higher than that of the container to avoid the condensation of the precursor within the line. The substrates were heated using a resistive heater. The temperature was measured and controlled by a heat controller with a type K thermocouple.

The substrates used for the PACVD Ta deposition consisted of polished AISI 4340 steel coupons. The substrates was diced with approximately 13×13 mm. V-groove patterned silicon wafers were employed to provide proof of concept that Ta coatings can be deposited uniformly and conformally. Prior to deposition, the substrates were cleaned in an ultrasonic bath with isopropanol, acetone, and methanol sequentially, rinsed with distilled water, and dried with clean nitrogen. After loading the substrates into the reactor, in-situ cleaning with excited molecular and atomic hydrogen produced by the RF plasma for 5–10 min was conducted to remove native oxide and organic contaminants. In this study, $TaCl_5$ with 10 sccm H_2 carrier gas was used while the flow rate of the H_2 reactant gas was 500 sccm. The precursor temperature investigated was in the range of 373–393 K. The deposition temperature and the total pressure were varied in the range of 553–733 K and 93–400 Pa, respectively. The RF power used to produce the plasma was varied in the range of 50–100 W.

Prior to carrying out the characterization work, all the coated samples were ultrasonically cleaned in methanol followed by acetone. For the cross sectional analysis of the Ta coatings, the specimens were cross-sectioned and mechanically polished using SiC with grit sizes down to 1200 followed by a polycrystalline diamond suspension with particle sizes down to 0.05 μm. The surface morphology and conformal coverage of the Ta coatings were investigated by using a field emission scanning electron microscopy (FE-SEM, LEO 1530 VP) on the surface and cross-sections of coatings deposited on steel coupons as well as silicon wafers. Energy dispersive X-ray spectroscopy (EDX, Oxford INCA Energy 400) was carried out for elemental analysis of the coatings. Atomic force microscopy (AFM, Nanoscope IIIA Multimode scanning probe microscope, Digital Instruments) in contact mode was employed to examine the topography and surface

Table 1
Summary of the deposition conditions for the CVD Ta coatings on steel substrates.

Group #	H_2 reactant (sccm)	H_2 carrier (sccm)	Pressure (Pa)	Deposition temp. (K)	RF (W)	Precursor temp. (K)	Distance (mm)[a]	Growth rate (nm/min)
1	500	10	267	673	60	393	40	3.9 ± 0.3
	500	10	267	703	60	393	40	5.2 ± 0.2
	500	10	267	733	60	393	40	5.9 ± 0.3
2	500	10	200	703	60	388	40	3.2 ± 0.3
	500	10	267	703	60	388	40	4.7 ± 0.5
3	500	10	267	703	60	383	40	4.5 ± 0.5
	500	10	400	703	60	383	40	1.8 ± 0.1
4	500	10	93	643	50	373	50	1.8 ± 0.1
	500	10	93	643	50	383	50	3.7 ± 0.1
5	500	20	267	733	60	393	40	8.9 ± 0.2

[a] Distance from electrode to substrate (see Fig. 1).