Surface & Coatings Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Deposition of copper thin films by plasma enhanced pulsed chemical vapor deposition for metallization of carbon fiber reinforced plastics

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ARTICLE INFO

Article history:
Received 31 October 2015
Revised 23 May 2016
Accepted in revised form 11 July 2016
Available online xxxx

Keywords:
CFRP
Copper film
Chemical vapor deposition

ABSTRACT

Metallization of carbon fiber reinforced plastic (CFRP) materials is a critical issue for protection against environmental attack and improvement of their electrical conductivity. In practice, the process should be preferably carried out below 150 °C to avoid epoxy resin decomposition. This work investigated a plasma enhanced pulse chemical vapor deposition process for copper thin film deposition at a temperature as low as 50 °C. Copper(I) di-isopropylacetamidinate was used as Cu precursor with high reactivity to H_2 plasma at low temperature. At certain experimental conditions (10 s Cu precursor pulse and 10 s H_2 plasma pulse, 100 °C), the Cu films deposited on CFRP were pure, continuous, with the resistivity of 4.4 μΩ cm. The influence of the deposition temperature on copper characteristics has been investigated.

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1. Introduction

In recent years, carbon fiber reinforced plastic (CFRP) materials have been used widely in the aerospace and aircraft industry due to their intrinsic characteristics of high stiffness, low weight, super corrosion resistance, great thermal and dimensional stability [1,2]. The density of CFRP is around 1.5 g/cm^3, half that of aluminum and more than five times lower than copper. As a result, CFRP offers, relative to the conventional metal materials, extensive weight savings. A waveguide antenna made of CFRP material needs a less powerful drive system. Moreover, radiating waveguides require cross sectional stability of ± 0.05 mm. Therefore, CFRP material is an efficient alternative for aluminum or copper due its excellent thermal and dimensional stability.

In the space environment, the exposure to the humidity, sand particle, high energy UV irradiation and aggressive chemical reagents makes spacecraft made of CFRP tend to crack and even fail, which dramatically shorten the life of the spacecraft [2,3]. Besides, the low electrical conductivity due to the resin matrix makes CFRP unsuitable for direct use as waveguide elements. So the metallization of CFRP surface is proposed for protection against environmental attack and improvement of its electrical conductivity.

Diverse methods, such as physical vapor deposition (PVD) and electro-deposition have been used previously to enhance CFRP conductivity [4,5], including the inner surface of the waveguide being coated with a highly conductive metallic layer. Although PVD technique is simple and straightforward, it cannot meet the requirements to deposit conformal films for high aspect ratio tubes because of its line-of-sight depositing flux and high sticking coefficient on most materials [6]. Electochemical deposition (ECD) is currently the preferred method for depositing bulk copper. However, ECD requires deposition of a thin metal seed layer about 20 nm before the plating process [7]. In order to deposit a good uniform and conformation film in high aspect ratio structures, techniques of chemical vapor deposition (CVD) and atomic layer deposition (ALD) have been developed in the last two decades. Regarding the metallization of CFRP by CVD and ALD, the epoxy resin will decompose if the deposition temperature is above 150 °C since CFRP material is the mixture of carbon fiber and epoxy resin. Therefore, in general, the thermal vapor deposition is unsuitable for Cu deposition on CFRP samples due to its usual reaction temperature of 200 °C.

To realize the low temperature deposition, a key issue to deposit Cu films is the precursor selection, which can greatly affect the vapor deposition processing conditions and the grown thin film qualities. Generally, copper precursors for CVD and ALD can be classified into two types: Cu(I) compounds including copper halides and copper amidinates, and Cu(II) compounds such as Cu(II) acetylacetonate [Cu(acac)$_2$],Cu(II)-1,1,1,5,5,5-hexafluoro-2,4-pentanedionate [Cu(hfac)$_2$] and Cu(II)-2,2,6,6-tetramethyl-3,5-heptandionate [Cu(thd)$_2$] [8,9]. Cu(II) compounds have several advantages such as easy synthesis and reasonable thermal stability but suffer from undesirable properties like low vapor pressure and limited reactivity. There is also a potential risk in that an incomplete reduction of these β-diketonates might occur, leading to residues of carbon, oxygen or fluorine in copper films. In comparison, CuCl and H_2 with the deposition temperature between 360 and 410 °C, and CuCl and Zn between 440 and 500 °C have been used to deposit Cu films. The low vapor pressure and high deposition temperature and corrosive hydrochloric acid by product from reduction to Cu metal severely limit the use of this Cu(I) compound as a viable Cu ALD

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http://dx.doi.org/10.1016/j.surfcoat.2016.07.029
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precursor. However, Cu(I) amidinates were described by Gordon and co-workers as the promising Cu precursors due to their high volatility and sufficient reactivity with H_2 [10]. Copper(I) di-isopropylacetamidinate $[Cu(AMD^{iPr2})]_2$ and Copper(I) di-sec-butyl acetamidinate $[Cu(AMD^{sBu2})]_2$ have been reported to deposit thin continuous Cu films on blanket Co surface [9,11].

Another issue to achieve low temperature Cu deposition is to use energetic plasma to enhance the reactivity of the co-reactant agent, which is also known as plasma enhanced CVD/ALD (PECVD/ALD). In 2004, Jezewski [12] reported the experimental study on Cu growth, using $Cu(tmhd)_2$ and hydrogen plasma, on SiO_2, Au and TaN_x substrates at the deposition temperature from 90 °C to 250 °C. The oxygen and carbon contents in the films were determined to be 35% and 1–3%, respectively. Niskanen [13] carried out copper deposition on glass and silicon substrates based on copper(II) 2,4-pentanedione ($Cu(acac)_2$) and hydrogen radicals generated by a surface-wave launcher plasma source. The saturated growth rate of Cu was measured to be 0.018 nm/cycle, containing approximately 11 at.% oxygen, 2 at.% hydrogen and 1 at.% carbon, respectively. In 2011, Moon et al. [14] studied the Cu seed layer on Ta/SiO_2 substrate employing Bis (1-dimethylamino-2-methyl-2-butoxy) copper (MABOC) and atomic hydrogen. At a reaction temperature of 150 °C, the resistivity of the deposited Cu film was 5.2 μΩ cm and the impurity content was below 5 at.%. Regarding copper deposition on CFRP substrates, there are no reports to be found up to now.

In general, PEALD is a very slow process, and the impurity contents are high in PECVD process. Here, the present work aims to deposit Cu films on CRFP samples using plasma enhanced pulse chemical vapor deposition (PEPCVD) technique. $[Cu(AMD^{iPr2})]_2$ was chosen as copper source due to its suitable physical and chemical properties. Compared to some other copper precursors, $[Cu(AMD^{iPr2})]_2$ is without oxygen element, which avoids the source of oxygen impurity. The influences of deposition parameters on Cu growth will be discussed.

2. Experimental

The experiments were conducted in a PEPCVD system shown schematically in Fig. 1(a). The reactor consists of a dielectric fused-silica tube (id. 40 mm), an aluminum half-cylinder placed along the axis of the reactor tube as the substrate supporter. Si (100) wafers and SiO_2 (300 nm)/Si were used as deposition substrates to characterize copper films, and CFRP tubes with different lengths were prepared to metallization. Since the copper film is deposited on the inner surface of CFRP tube, it is impossible to character the thin film. Hence, small strips cut from slides were positioned inside the tubes at different places for testing and analysis of copper films. The RF power supply source is capable of supplying 13.56 MHz frequency and 0–500 W variable power, inductively coupled through a 50 mm diameter, 3 turns, copper coil that surrounded the fused-silica tube.

The temperature of the reactor was controlled by a temperature-programmed controller and a heating element embedded in the half-cylinder under the substrates. The average of T_{out} (outside temperature of the fused-silica tube) and T_c (the center temperature measured from the central half-cylinder) were taken as the deposition temperature, measured by the thermocouples placed on the outside tube wall and in the substrate supporter. T_c was typically kept ~10 °C higher than T_{out}. $Cu(AMD^{iPr2})$ was bubbled at 90 °C by N_2 carrier gas flow, which was kept constant at 50 standard cubic centimeters per minute (sccm) during Cu precursor pulse. H_2 was employed as reducing agent, flowed continuously with 50 sccm flow rate even though copper precursor was delivered. The copper pulsed CVD cycle consists of 10 s $Cu(AMD^{iPr2})$ pulse, and 10 s H_2 plasma pulse, shown in Fig. 1(b).

The thickness of the deposited Cu films was measured by step profilometry (Veeco, Dektak 150). The film surface morphology of the films was examined by scanning electron microscopy (SEM) (Hitachi, SU8020) and atomic force microscopy (AFM) (Veeco, diInnova). The crystalline phase of the deposited film was evaluated by X-ray diffraction (XRD) (Rigaku, D/max-2200 PC). The film chemical composition was determined by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific, K-Alpha). The sheet resistance of the films was measured by a four-point probe station (RTS-8).

3. Results and discussion

For the process of PEPCVD, characterizations of copper films deposited on Si (100) wafers and SiO_2 (300 nm)/Si were firstly studied. Fig. 2(a) shows the film thickness grown on silicon as a function of the pulsed CVD cycles (10 s $[Cu(AMD^{iPr2})]_2$ pulse and 10 s H_2 plasma pulse, $T_c = 100$ °C). The deposition rate can be estimated from the

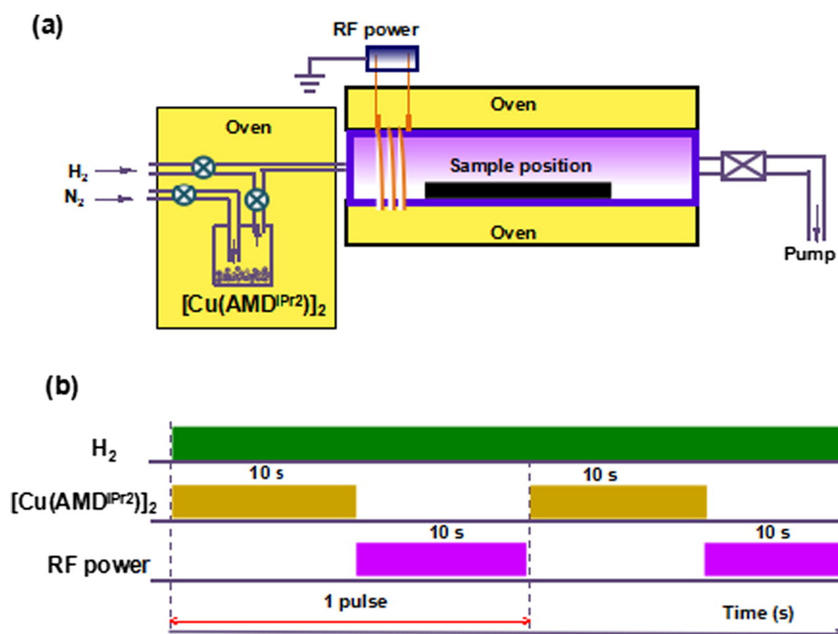

Fig. 1. (a) Schematic of the PEPCVD reactor. (b) Schematic layout of the PEPCVD pulse for Cu deposition.

Please cite this article as: Z. Guo, et al., Surf. Coat. Technol. (2016), http://dx.doi.org/10.1016/j.surfcoat.2016.07.029

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