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Preparation and characterization of oxidized electrolytic copper powder and its dielectric properties at microwave frequency

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ABSTRACT

The electrolytic copper powder oxidized in air at various temperatures is tested to understand the effect of oxidation on the dielectric properties at the microwave frequency for the use in the high frequency semiconductor equipments. The X-ray diffraction for these oxidized copper powders is performed to identify the different oxide phases and its crystal structures. The morphology of the oxidized and pure copper particles has been observed using the scanning electron microscopy. The EDX analysis has been carried out to determine the oxide phases. The different oxide phases present in the oxidized samples are confirmed from Raman spectra analysis. The dielectric properties of these powdered samples are evaluated using the transmission coefficient data measured by the vector network analyzer in the X-band of microwave frequency range. The dielectric constant and the effective conductivity (dielectric loss) are increased with the increase in powder density of pure as well as oxidized copper powders. However, the real part of the complex permittivity and the effective conductivity (dielectric loss) are getting reduced with increasing the volume fraction of oxide phases. The prepared dendrite shaped oxidized electrolytic copper is the unique candidate in the preparation of composite which is used as a heat-radiating board of the semiconductor equipment, an electrostatic adsorption device, and a dielectric board of the electrostatic adsorption device.

1. Introduction

In electronics industry, the bulk metals are commonly used in a wide number of applications such as the design of various types of connectors [1,2], for the electromagnetic (EM) shielding devices [3], and for the protection and proper grounding of the sophisticated devices [4]. In the higher frequency range, the metal films are usually preferred for various microwave applications due to the smaller skin depth [5]. In recent years, the metal powders and their associated composites are being used in lieu of bulk metals for various high frequency applications mainly caused by long term reliability, lower cost and light weight [6–8]. The lattice defects free granular metals and their oxides are employed for a variety of applications [7,9,10]. For instance, titanium and its alloys are used in medical and dental fields [11], metallic oxides (like ZnO, MgO and CaO) are used for antibacterial activities [12], and the metallic powder (like Co) is used for metallic coating using plasma spray technique [13].

The copper oxides are helpful reference systems for the study of complex cuprates, the majority of which play an important role in organic chemistry and show high-T_c superconductivity. The Cu_2O is of particular interest since it is one of the most frequently used metal oxide powders that has a wide range of potential applications, attributable to the environmental acceptability, low cost, non-toxicity, and abundance [14]. For instance, the Cu_2O is a p-type direct band gap semiconductor with energy band gap of 2.0–2.2 eV, which is the promising material for solar energy converting devices [15], but it can also be used as the photocatalyst [16,17], antibacterial materials [18], fuel cell materials [19], gas sensor [20], antifouling coating materials [21] and prominently in the preparation of composite for being used as heat-radiating board in the semiconductor equipments [22]. There are several methods to synthesize the cuprous oxide including thermal oxidation [23], electrolysis [24], hydrothermal synthesis [25], reduction of cupric salts [26] and γ-irradiation [27].

For making use in the semiconductor equipment, it is interested to explore the dielectric properties of oxidized copper powder that has the cuprous oxide phase, at higher frequency ranges. The present article is intended to report the oxidation of copper powder at different temperatures for the development of oxide phases, and the effect of oxidation on the microwave dielectric properties. The powders that have been oxidized at different temperatures are analyzed from structural, morphological, Raman and microwave dielectric point of view to show its strong candidacy in high frequency semiconductor devices.

The main aim of our paper is to study the dielectric properties of oxidized electrolytic copper powder from the microwave point of view in addition to their microstructural properties. This kind of detailed study

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explores the possibility of using Cu_2O and CuO for the design of customized electromagnetic absorbers. To the best of author's knowledge, this kind of systematic study regarding the design of microwave absorbers by changing the Cu_2O and CuO in various proportions has not been done in the past.

2. Experimental

2.1. Sample preparation

The electrolytic copper metal powder (300 meshes LD) was purchased from the Samir Tech-Chem. Pvt. Ltd. For the comparative studies, the following sets of powdered samples have been considered:

(i) As-received copper powder (purity ~ 99.5%),
(ii) Pulverized copper oxidized at room temperature, and
(iii) Pulverized copper oxidized at 200 °C and 400 °C in the presence of ambient air.

For the 2nd case, the copper powders are spread in a Petri dish and are kept in open atmosphere for 48 h. The presence of atmospheric moisture helped to get the pure copper powder oxidized which became brownish red. In the 3rd case of preparation, the copper metal powder has been placed in the alumina boat and inserted inside the electric furnace at 200 °C and 400 °C each for 4 h, in air atmosphere. After removing it from the electrical furnace, the powder turned into black-brownish solid which was then crushed into fine powder using mortar and pestle.

2.2. Characterization techniques

The crystal structure of copper and oxidized samples is recorded by X-ray diffraction (XRD) using a Thermo Electron ARL X'TRA, in 2θ range of 20–80° with Cu-K_α radiation, scan rate of 2°/min, steps of 0.05° and time constant of 1 s. The surface morphology is analyzed with the help of scanning electron microscopy (SEM) using a model FEI QUANTA-200, M/S FBI, Germany. The Raman spectra are characterized by Horiba-Jobin Yvon equipment (model Lab RAM HR800) with a resolution of 1 cm^{-1}, excitation wavelength 632.8 nm (He–Ne laser) and power 1 mW.

In order to measure the microwave dielectric parameters of the powder samples, an X-band rectangular cavity is fabricated and the sample holder has been specially designed for holding the powdered sample inside the cavity. The fabricated cavity along with the waveguide to coax adapter is connected with the vector network analyzer (VNA) of Keysight Technologies. The fabricated cavity is operating in the TE_{107} mode. The resonant frequency and the quality factor of the fabricated cavity when loaded with empty sample holder are f_{sh} (9.4735 GHz) and Q_{sh} (2078.7), respectively. The complex permittivity is calculated using the cavity perturbation formula [28] as given by

$$\varepsilon_r' = 1 + \frac{V_c}{AV_s}\left(\frac{f_{sh}-f_s}{f_s}\right) \tag{1}$$

$$\varepsilon_r'' = \frac{V_c}{BV_s}\left(\frac{1}{Q_s}-\frac{1}{Q_{sh}}\right) \tag{2}$$

where, f_s and Q_s are the resonating frequency and the quality factor of the loaded cavity of volume V_c; ε_r' and ε_r'' are the real and imaginary parts of the complex permittivity of the test sample of volume V_s, respectively. The symbols A and B are the shape factor coefficients which depend on the shape and size of sample holder and the powder density. The determination of these coefficients is not very straightforward using the analytical procedures, and hence the numerical optimization technique using the full wave electromagnetic software, the CST Studio is used for the analysis as explained elsewhere [29].

2.3. Calculation of powder density

The effective dielectric properties of the metal powders are function of the bulk electrical properties of the corresponding metal as well as their volume density. In this paper, a new module is proposed to vary the density of copper powders during the microwave measurement, which requires the especially designed sample holder with the hydraulic piston as illustrated in Fig. 1. This module is then integrated with the waveguide cavity setup for the microwave characterization using the vector network analyzer (VNA).

It is to be noted here that the volume of bulk particulates remains unchanged for a given amount of powder during the whole process. However, the total powder volume ($V_T = \pi r^2 h$) is varying here using the integrated hydraulic piston, which actually changes the powder volume and density. Therefore, by measuring only the powder level (h) inside the sample holder of inner radius (r), the powder volume density (ρ_{powder}) of various copper powders are calculated using the following expression

$$\rho_{powder} = \rho_{air}\left[1 + \nu_m\left\{\frac{\rho_m}{\rho_{air}} - 1\right\}\right] \tag{3}$$

where, $\nu_m = \frac{C}{h}$ and $C = \frac{m}{\pi r^2 \rho_m}$.

The term C is constant for given metallic powder (as m is unchanged during measurement). The symbols ρ_m and ρ_{air} are the densities of the bulk metal and the air, respectively, while ν_m represents the volume ratio of bulk particulates to the total powder volume.

3. Results and discussions

3.1. X-ray diffraction analysis

The X-ray diffraction patterns of pure electrolytic copper powder and oxidized electrolytic copper powders are shown in Fig. 2. The XRD pattern of pure electrolytic copper powder shows that the peak intensities lie at angle 2θ = 43.32°, 50.46°, and 74.12° (Fig. 2a), which are exactly matched with ICSD reference pattern code; 01-085-1326 (JCPDS File No. 4-836) with corresponding reflection planes (111), (200), and (220), respectively [30]. It is to be noted that the pure copper powder has the face centered cubic (FCC) crystal structure with space group Fm3m. The XRD pattern of the copper powder oxidized at room temperature is shown in Fig. 2b, where some low intensity peaks other than

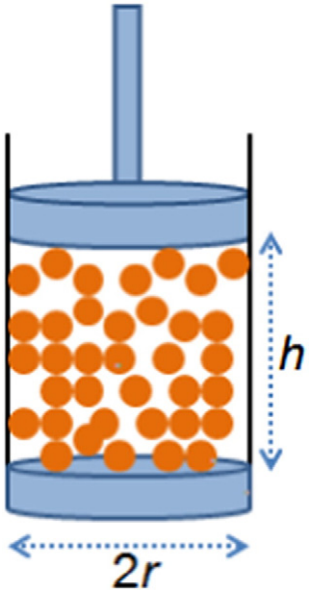

Fig. 1. Illustration of the especially designed sample holder filled with copper powder.