



Electrodeposition of bismuth telluride thin films containing silica nanoparticles for thermoelectric applications



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ABSTRACT

The electrodeposition of bismuth telluride (Bi₂Te₃) with incorporated silica nanoparticles (diameter = 16 nm) was studied in ethylene glycol using a rotating disk electrode. "By matching the refractive index of the silica nanoparticles to the refractive index of the electrolyte i.e. "refractive index matching", the attractive van der Waals force between particles was minimized. Refractive index matching was used to avoid agglomeration of the silica particles in solution due to the attractive van der Waals forces and resulted in Bi₂Te₃ coatings that contain up to 8 vol% of individual silica particles as verified by TEM. The concentration of the incorporated silica nanoparticles was found to be influenced by several parameters: the applied current density, rotation speeds and silica concentration in the electrolyte. A model was developed to predict the amount of incorporated particles. The effect of each parameter was predicted by this model and verified experimentally. The Seebeck coefficient and thermal diffusivity of bismuth telluride films with and without silica nanoparticles were measured.

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1. Introduction

Thermoelectric devices such as thermoelectric coolers and thermoelectric generators have become more popular in recent years [1–5]. The conversion efficiency of a thermoelectric device depends on the design of the device and the performance of the thermoelectric materials used [6]. The performance of a thermoelectric material can be evaluated by the dimensionless figure of merit ZT :

$$ZT = \frac{S^2 \sigma}{\kappa} T \quad (1)$$

where T is the temperature [K], S is the Seebeck coefficient [V K⁻¹], σ is the specific electrical conductivity [$\Omega^{-1} \text{m}^{-1}$], and κ is the specific thermal conductivity [W m⁻¹K⁻¹]. To increase the conversion efficiency, a high ZT number is desired. High ZT values are observed for semiconductors with a low thermal conductivity (κ) and a high power factor ($\alpha^2 \sigma$). Incorporation of nanoparticles in thermoelectric materials is one of the methods to improve the ZT

number. Kim *et al.* embedded ErAs nanoparticles in an In_{0.53}Ge_{0.47}As matrix and successfully achieved almost 50% reduction in thermal conductivity and more than a factor of two increase in the ZT number [7]. Kundun *et al.* found that nanoparticles with higher specific density reduce the thermal conductivity more efficiently than lighter nanoparticles due to their higher scattering rate of low frequency phonons [8]. They also predicted an optimized radius of particles around 10 nm to minimize the thermal conductivity of Si-Ge alloys [8]. However, a recent computational study on the effect of the particle size on the thermal conductivity indicates that incorporation of particles with a few well-chosen radii instead of a single radius is the most efficient way to minimize the thermal conductivity [9]. In some cases nanoparticles can even enhance the power factor of the material by increasing the Seebeck coefficient [10] or increasing the electrical conductivity [11].

Electrodeposition is a cost-efficient technique to prepare thin films as well as thin films that contain particles [12]. Particles are added and suspended in the electrolyte and some of the particles are incorporated with the reduced metal ions in the deposit. In the electrolyte, the forces between the particles mutually and between the particles and the electrode play a very important role during

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electrodeposition and they determine whether particles can be embedded in the coating and whether the particles will agglomerate and hence embed as agglomerates or not [13,14]. Attractive forces between the matrix material and the particles are favored. On the other hand, repulsive forces between particles are desired to prevent agglomeration and to obtain individual particles in the matrix. Fransaer and coworkers described the different external forces acting on a particle in an electrolyte during electrodeposition [13–15]. The stability of colloids in an electrolyte is largely governed by the electrostatic double layer repulsion and the van der Waals force, which is always attractive between identical particles, as first laid out in the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [16]. However, in concentrated electrolytes as the ones used in electrodeposition, the double layer repulsion becomes almost completely annihilated as the Debye length, which is a measure of the decay length of the double layer force, is inversely proportional to the ionic strength of the electrolyte. This implies that the stability of nanoparticles in the electrolyte is dominated by the attractive van der Waals interaction. The van der Waals attraction potential between two spherical particles of radius a_p can be written as [17]:

$$V_{\text{vdw}} = -\frac{A}{6} \left[\frac{2a_p^2}{h^2 - 4a_p^2} + \frac{2a_p^2}{h^2} + \ln \left(\frac{h^2 - 4a_p^2}{h^2} \right) \right] \quad (2)$$

where A is the Hamaker constant, which is the measure of the dispersion interaction of two materials across a third material [J], a_p is the radius of the particles [m], and h is the center-to-center distance between two particles [m]. A positive Hamaker constant indicates the van der Waals force is attractive, while a negative Hamaker constant means the van der Waals force is repulsive. The Hamaker constant of identical particles across a media can be estimated from the Lifshitz theory [16,18,19]:

$$A \approx \frac{3}{4} k_{\text{BT}} \left(\frac{\epsilon_p - \epsilon_e(\text{electrolyte})}{\epsilon_p + \epsilon_e} \right)^2 + \frac{3h\nu_e (n_p^2 - n_e^2)^2}{16\sqrt{2} (n_p^2 + n_e^2)^3} \quad (3)$$

where n_p , n_e are the refractive indices of the particles and of the electrolyte [–] respectively; k_{B} is the Boltzmann constant [$1.3806 \times 10^{-23} \text{ J K}^{-1}$]; T is the temperature [K]; ϵ_p and ϵ_e are the static relative dielectric constants of the particle and the electrolyte [–] respectively; h is the Planck constant [$6.626 \times 10^{-34} \text{ J s}^{-1}$]; ν_e is the main electronic absorption frequency in the UV [s^{-1}]. The Hamaker constant between identical material is always positive, which means the van der Waals force between identical particles in an electrolyte is always attractive. The first term on the right-hand side cannot exceed $\frac{3}{4} k_{\text{BT}}$ which is about $3 \times 10^{-21} \text{ J}$ at 300 K and the second term is typically in the order of 10^{-19} J [16]. The contribution of the first term to the Hamaker constant is very small ($\sim 3\%$) [16]. To minimize the attractive force between the particles in a suspension, the Hamaker constant should be minimized by making the second term on the right hand side of eq. (3) as small as possible. This can be achieved if the refractive index of the particles equals the refractive index of the electrolyte (i.e. *refractive index matching*) [20,21].

Besides the electrostatic force and the van der Waals force, the hydration force which is a short-range repulsive force also has been shown to play an important role in the electrodeposition of particles [22,14]. The hydration force is due to the polarization (or hydrogen bonding) of water molecules near a solid surface in contact with water, which results in a thin layer of water called hydration layer. Ion transport was proven to occur in this hydration layer, resulting in the electrodeposition of metal underneath particles in contact with an electrode [14]. This hydration layer impedes the deposition of hydrophilic particles like SiO_2 with metals from aqueous solutions. Hence, the codeposition of

hydrophilic particles like silica is only feasible from non-aqueous electrolytes that contain no water [23,24] or by making the silica particles hydrophobic [25].

Bismuth telluride (Bi_2Te_3) is an important thermoelectric materials because it has the best thermoelectric performance at room temperature [26,27]. Electrodeposition of bismuth telluride thin films from aqueous solutions has been extensively studied in aqueous solutions [28–31]. However, the solubility of HTeO_2^+ ions in aqueous solutions is very limited even at very low pH [28,32]. Organic solvents show some advantages for the electrodeposition of bismuth and tellurium. Both $\text{Bi}(\text{NO}_3)_3$ and TeCl_4 have high solubilities in ethylene glycol and dimethyl sulfoxide [33,34]. In ethylene glycol solutions containing only nitrate salts, the film composition can be controlled much more easily due to the equilibrium alloy deposition behavior [35].

In this paper, Bi_2Te_3 films containing silica nanoparticles were electrodeposited from chloride-free ethylene glycol solutions. Silica nanoparticles stably dispersed in ethylene glycol solutions with high metal ion concentrations and could be deposited in the films as individual particles instead of agglomerates due to the refractive index matching of the nanoparticles and the electrolyte. In order to understand the effects of deposition conditions on silica incorporation, the effects of current density, rotation rate and silica concentration in the electrolyte were studied both experimentally and theoretically.

2. Experimental

Ethylene glycol (Alfa Aesar, 99%), ethylene glycol containing 200 g L^{-1} amorphous silica (SiO_2) nanoparticles (diameter = 10–15 nm) (EG-ST, Nissan Chemicals), TeCl_4 (Alfa Aesar, >99%), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Alfa Aesar, >98%), LiNO_3 (Sigma-Aldrich, 99%), AgNO_3 (Chempur, 99%), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (Riedel-deHaën, 99%), ferrocene (Acros Organics, 98%), ferrocenium hexafluorophosphate (Sigma-Aldrich, 97%), TiO_2 nanoparticles (Marketch, 30 nm, 99.9%) were used in the experiments.

An ethylene glycol solution containing 0.5 M $\text{Te}(\text{NO}_3)_4$ was prepared by mixing ethylene glycol solution containing 1 M TeCl_4 with a solution containing 4 M AgNO_3 . The AgCl precipitate was removed by filtering and the excess of silver ions in solution was removed by electrodeposition [35]. Ethylene glycol, ethylene glycol containing 200 g L^{-1} silica and 0.5 M $\text{Te}(\text{NO}_3)_4$ and 0.5 M $\text{Bi}(\text{NO}_3)_3$ in ethylene glycol were dried under vacuum (3 mbar) for about 24 h. Ethylene glycol was further dried using anhydrous Na_2SO_4 . Anhydrous Na_2SO_4 absorbs water in ethylene glycol forming $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Anhydrous Na_2SO_4 was obtained by drying $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (Riedel-deHaën, 99%) at 150 °C in an oven for about 12 h. The electrolytes containing silica nanoparticles were prepared by mixing ethylene glycol containing 200 g L^{-1} silica nanoparticles with ethylene glycol solutions. 0.5 M LiNO_3 (Sigma-Aldrich, 99%) was added to all the solutions to increase the ionic conductivity.

All the electrochemical experiments were carried out in an argon-filled glove box (oxygen content was below 0.5 ppm and water content was below 0.1 ppm). A three-electrode set-up was used. The reference electrode was a glass tube with a porous ceramic plug in the bottom filled with an ethylene glycol solution with 2 mM ferrocene (Fc) and 2 mM ferrocenium hexafluorophosphate (Fc^+) and 1 M LiNO_3 . The potential of the Fc/Fc^+ electrode was compared with the $\text{Ag}/\text{AgCl}/3 \text{ M KCl}$ electrode in a 3 M KCl solution at room temperature. The potential of the Fc/Fc^+ electrode was +0.29 V vs. $\text{Ag}/\text{AgCl}/3 \text{ M KCl}$ electrode. In this paper, all potentials were converted with respect to the standard hydrogen electrode (SHE). A platinum coil was used as counter electrode. The films were deposited on gold-coated silicon wafers

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