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Influence of titanium nitride interlayer on the morphology, structure and electrochemical performance of magnetron-sputtered lithium iron phosphate thin films

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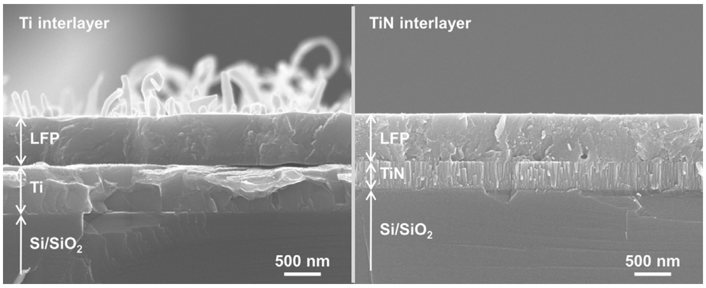
HIGHLIGHTS

- Formation of iron rich surface particles due to Ti and LFP interdiffusion.
- TiN interlayer effectively blocks interdiffusion.
- Very smooth and homogeneous surfaces are obtained with TiN interlayer.
- Crystallization behaviour is improved by TiN interlayer.

GRAPHICAL ABSTRACT



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ABSTRACT

Pure $LiFePO_4$ (LFP) thin films with different thicknesses are deposited at room temperature by a radio frequency (RF) magnetron-sputtering process. Ti foils with and without titanium nitride (TiN) coating as well as thermally oxidized Si wafers coated with Ti or TiN are used as substrates. In a subsequent annealing step, $LiFePO_4$ thin films are crystallized at 500 °C. The interaction between Ti and $LiFePO_4$ as well as between TiN and $LiFePO_4$ is characterized by means of X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray analysis (EDX), secondary ion mass spectrometry (SIMS), cyclic voltammetry (CV) and galvanostatic measurements. A severe diffusion of Ti into $LiFePO_4$ is found and leading to the formation of impurity phases which resulting in disturbing crystallization behaviour and rough surfaces. Moreover, 80 nm $LiFePO_4$ thin films do not show the desired electrochemical characteristics when they are deposited on Ti foils directly. By using a TiN interlayer, the diffusion of Ti into $LiFePO_4$ can be blocked resulting in smooth morphologies and improving crystallisation behaviour. Impurity phases do not develop and all samples exhibit the expected electrochemical characteristics. Therefore, TiN is a promising candidate for the use as a current collector in all-solid-state batteries with $LiFePO_4$ electrodes.

1. Introduction

In recent times all-solid-state batteries attract much attention due to their good cyclability, long lifetime and especially high inherent safety [1]. A promising cathode material for the

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application in all-solid-state batteries is LFP. It is an environmental benign, non-toxic and low-cost material with a high theoretical capacity of 170 mAh g^{-1} [2,3].

The high inherent safety of an all-solid-state battery originates from the replacement of the organic liquid electrolyte by a non-flammable and less reactive solid electrolyte. However, in general, solid electrolytes have a lower ionic conductivity. The lower ionic conductivity would lead to lower rate capabilities if solid electrolytes with comparable thickness to that of liquid one were used. Therefore, one approach to circumvent lower rate capabilities is to use thin film solid electrolytes in the micrometre thickness range.

A crucial point in fabricating all-solid-state batteries is the coverage and adherence between the single layers. A working battery can only be obtained if any electronic contacts between anode and cathode are avoided. Since the distance between the electrodes is in the micrometre range, a complete coverage of the electrodes without any defects has to be ensured by the solid electrolyte. Furthermore, a good adherence between the solid electrolyte and the electrodes is needed to provide a good Li^+-ion transport between the layers. These requirements can be fulfilled by using electrodes with smooth surfaces.

For this reason, thin film electrodes are appropriate candidates for all-solid-state batteries because they can be prepared with smooth surfaces by a variety of thin film techniques like physical vapour deposition (PVD), chemical vapour deposition (CVD), or sol–gel methods [4]. Some of these thin film techniques like radio frequency (RF) sputtering [5–12], pulsed laser deposition (PLD) [13–21], electrostatic spray deposition (ESD) [22], and aerosol deposition [23] have already been successfully applied to prepare LFP thin films.

All of the LFP thin films made by PVD techniques have to be deposited at elevated temperature or need a subsequent heat treatment to get a crystalline structure with an improved electrochemical performance [9,21]. Such a heat treatment can intensify interdiffusion as shown by Chiu et al. for LFP thin films on substrates with a titanium interlayer [12]. The effect of interdiffusion between substrate and LFP film was also observed by Legrand et al. on MgO substrates [20]. In addition, this group reported the formation of iron-rich protuberances on the surface of the LFP thin films, which was developed as a consequence of the diffusion of Mg into LFP [18].

For the fabrication of all-solid-state thin film batteries, the formation of protuberances has to be avoided, because rough surfaces cannot be homogeneously coated with a solid electrolyte by PVD techniques. One attempt to avoid protuberances generated by interdiffusion processes can be made by using a diffusion barrier layer. In this paper TiN is proposed as an appropriate barrier material because it is chemically more stable than pure Ti and has a sufficient high conductivity to sustain electron transport to the cathode [24,25]. Furthermore, the aim focuses on characterizing the interaction between the deposited LFP thin film and the underlying layer and how it affects resulting structure, morphology and performance.

2. Experimental

2.1. Target and thin film preparation

Pure $LiFePO_4$ powder was prepared via a solid state reaction. $FeC_2O_4 \cdot 2H_2O$ and LiH_2PO_4 were used as starting powders in stoichiometric ratios. The starting powders were thoroughly mixed by a ball milling process by using yttrium stabilized zirconia balls for 24 h in ethanol. The mixed solution was dried and finely grinded in a mortar. In two subsequent heating steps, the powder was calcinated at 600 °C for 5 h in air and reduced then at 650 °C for 5 h in Argon with 4 vol.-% of hydrogen (Ar/H_2) atmosphere. The crystal structure and composition of the obtained LFP powder were checked by XRD and inductively coupled plasma - optical emission spectroscopy (ICP-OES), respectively (not shown).

Thermally oxidized silicon wafers and Ti foils were used as substrates. The Ti foil had a thickness of 125 μm. Ti was chosen as substrate material because it is a light-weight current collector with a high melting point at reasonable costs. In the first step, the substrates were cleaned with an organic solvent in an ultrasonic bath. Then, all substrates were sputter-etched prior to the deposition. Afterwards, the substrates were transferred to the deposition chamber without breaking the vacuum.

TiN interlayers with a thickness of 400 nm were made by an unbalanced direct current (DC) magnetron sputtering process using a Ti target on thermally oxidized Si wafers and on Ti foil. The deposition was conducted at room temperature in an Ar/N_2 mixture with 25 vol.% of nitrogen at a pressure of $5 \cdot 10^{-3}$ mbar for 40 min. The discharge power was kept at 500 W. Ti interlayers on thermally oxidized Si wafers were also made by an unbalanced DC magnetron process using a Ti target. The deposition was conducted at 500 °C in pure Ar atmosphere at a pressure of $5 \cdot 10^{-3}$ mbar. The Ti interlayer was deposited for 40 min at a discharge power of 500 W. The obtained film thickness was 650 nm.

The LFP thin films with thicknesses ranging from 80 nm to 640 nm were prepared by an unbalanced RF magnetron sputtering process. The LFP target with a diameter of 250 mm was made by cold pressing the LFP powder on a copper backing plate. The LFP was sputtered at a power of 600 W in pure Ar atmosphere at a gas flow of 20 sccm and a pressure of $5 \cdot 10^{-3}$ mbar for 0.5 h–4 h. The depositions were conducted at room temperature. The LFP thin films were subsequently crystallized at 500 °C in the deposition chamber. The samples were annealed for 2 h in Ar atmosphere at a pressure of $1 \cdot 10^{-2}$ mbar. The heating rate and cooling rate was kept at 3 K/min.

2.2. Characterization methods

The crystal structure was analysed with a Bruker D4 Endeavour (Bruker AXS, Germany) using Cu Kα radiation. Images of the

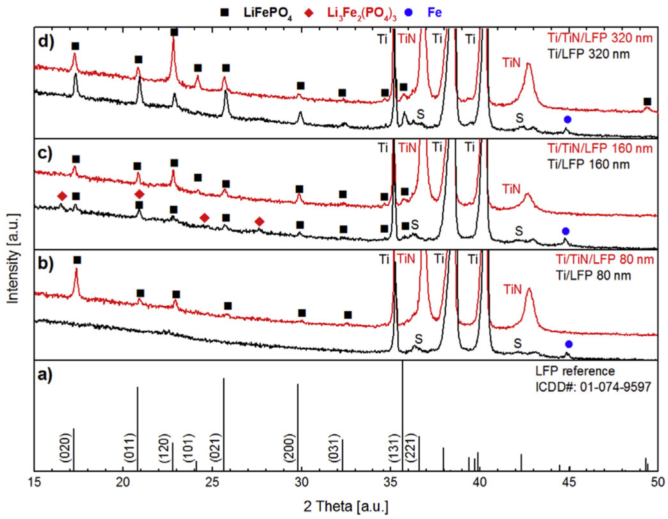

Fig. 1. XRD patterns of annealed LFP thin films with a thickness of b) 80 nm, c) 160 nm, and d) 320 nm on Ti (black) and Ti/TiN (red). The annealing temperature was 500 °C. The reference positions of LFP are depicted in a). The reflections with the highest intensities are labeld according to the Pnmb space group. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)