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Structural Analysis of Submicrometer LiCoO₂ Films

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Submicrometer LiCoO₂ films were prepared with pulsed laser deposition (PLD) and rf sputtering using stoichiometric targets. The influences of both substrate material and annealing procedure on the polycrystalline microstructure of the LiCoO₂ films were investigated. XRD analysis revealed strong preferential orientation: annealed films deposited with PLD had their (00 l) planes parallel to the surface, while rf sputtered films had their (110) planes in this orientation. The rf-film also developed the (003) reflection typical of PLD-films, but only after prolonged annealing at 600°C. The degree of preferential orientation is influenced significantly by the annealing procedure and only little by the substrate material and the thickness of the deposited film. Pulsed laser deposition on an rf-sputtered seed layer revealed the PLD-film reflections. Extinction of the otherwise dominating (003) reflection indicated a random cationic distribution in LiCoO₂ with an NaCl-type structure.

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The lithium intercalation ability of LiCoO₂ was discovered 20 years ago by Goodenough and has been exploited by Sony with the introduction of their rechargeable C/LiCoO₂ battery in 1991. Presently, this technology finds large-scale commercial application as a power source for numerous handheld devices. Extensive research has been conducted to explore alternative materials, which are more cost effective and less toxic.¹ Until now, lithium cobalt oxide based electrodes exhibit superior properties in terms of cycle stability and energy density, a favorable combination for a reliable power source.^{2,3}

There is a growing interest in the production of secondary lithium batteries of smaller dimensions; microbatteries are very suitable to provide backup power for on-chip static memory modules. Integrated memory is encountered frequently due to a growing tendency in the microelectronics industry toward complete integration of all functions onto a single chip designed for one specific purpose. For example, a motor controller chip will contain everything from controller to the power regulation in one module called a multichip module (MCM). The functions can subsequently be implemented on a separate silicon substrate, interconnected, and stacked in a single housing.⁴ The addition of a single microbattery allows the digital memory states to remain unaffected during power failure or long time storage.

The common composite powder electrodes are unsuitable for microbattery application due to their porosity and the necessity for additives. The indistinct characteristics of powder-based electrodes also make modeling of the electrochemical intercalation behavior difficult. The present paper describes preparation and properties of dense, submicron films of polycrystalline LiCoO₂ on a silicon wafer with pulsed laser deposition (PLD) and rf sputtering. The well-defined composition, microstructure, and dimensions of the deposited layers make these samples suitable for fundamental electrochemical studies of the lithium intercalation process. Eventually, these films could find an application as a positive electrode in microbattery stacks. In this paper we provide a structural characterization of the LiCoO₂ films in all stages of preparation from deposition to annealing treatment. The favorable electrochemical properties of the LiCoO₂ films will be published in a forthcoming paper.

Experimental

Thin film deposition.—Submicrometer LiCoO₂ films were produced with pulsed laser deposition and rf sputtering using identical LiCoO₂ targets prepared by solid-state reaction. The composition was analyzed and proved to be stoichiometric.

In PLD a 193 nm ArF excimer laser was operated at 5 Hz repetition rate and focused to a beam intensity of 2 J cm⁻². Ablation was performed with a counter rotating target and substrate, located at 6 cm distance from each other. A background pressure of 0.2 mbar *p*_{O₂} was maintained. At these conditions the deposition rate was approximately 20 Å min⁻¹. The substrate holder could be heated to temperatures as high as 700°C. The substrate temperature during deposition was 300°C. *In situ* annealing was performed by increasing the temperature to 600°C for 30 min with 5°C min⁻¹. After cooling to room temperature the samples were exposed to the ambient.

RF sputtering conditions were substrate temperature, 300°C; argon-oxygen background pressure of 7 mTorr in 3:1 ratio; rf power, 50 W; and target-to-substrate distance, 6 cm. At these conditions the growth rate of the oxide layer was of the order of 5 Å/min⁻¹. Annealing treatment of all rf-sputtered samples was performed *ex situ*. Samples were heated with 2°C min⁻¹ to 400 or 600°C in stagnant air or in a constant gas flow containing 90% O₂/10% N₂ with a flow of 60 mL min⁻¹ STP. Typical annealing times were 30 or 180 min and are referred to as short and prolonged annealing treatment, respectively. Rapid thermal annealing (RTA) experiments were conducted in nitrogen ambient in a commercial STEAG SHS1000 machine as described by van de Leest *et al.*⁵ In this case the annealing time was 1 min and the applied heating and cooling rate was 10°C s⁻¹.

Silicon wafers (6 in. diam, (100) orientation) served as substrate material for both deposition techniques. The polished surface was ion-implanted with antimony to obtain n-type electronic conductivity. The wafer was then laser cut into 15 mm diam disk. The back side and rim of these disks were covered with 0.15 µm aluminum using rf sputtering. This metallic film served as electrical back side contact for electrochemical measurements, connecting the probe with the conducting silicon. In several cases an additional aluminum film (0.15 µm) was sputtered as the current collector together with an adhesion layer of 50 Å titanium prior to deposition of the LiCoO₂ film. Note that this substrate stack is subjected to the same temperature program as the LiCoO₂ film. The use of aluminum (as the current collector) limits the upper annealing temperature to its melting point of 660.4°C. Even at temperatures below this value one must be aware of possible interdiffusion of soluble species in the

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individual stack layers. The time and temperature window of the thin film annealing process is therefore limited.

Structural analysis.—The crystal structure of the submicrometer film was analyzed with X-ray diffraction (XRD) using Cu K α at room temperature with a Philips PW 1800 diffractometer fitted with a spinning sample holder and an automatic divergence slit. Visualization of the film surface morphology was performed using a JEOL JSM 5800 scanning electron microscope (SEM). A Philips CM30ST, operated at 300 kV, accommodated transmission electron microscopy (TEM) analysis on cross sections of rf film prepared with focused ion beam (FIB) thinning.

Results and Discussion

Structural characterization.—Generally, the LiCoO₂ host intercalation matrix is regarded to be derived from the NaCl structure. The structure is rhombohedral (space group $R\bar{3}m$) with atoms in the following positions: cobalt atoms in 3a sites (0, 0, 0), lithium atoms in 3b (0, 0, 1/2), and oxygen in 6c sites $\pm$ (0, 0, z) with $z \approx 0.25$. Cobalt and lithium alternately occupy octahedral sites between adjacent close-packed planes of oxygen. The hexagonal cross section (110) is shown in Fig. 1. This ordered structure is known as the high-temperature (HT) phase of LiCoO₂, since it develops during synthesis or annealing treatment at temperatures above 600°C. Once formed it remains stable at room temperature. The so-called low-temperature (LT) modification is produced with low temperature synthesis methods and is slightly disordered; it comprises 6% of the cobalt ions in lithium sites. LT-LiCoO₂ transforms into HT-LiCoO₂ upon annealing at temperatures around 600°C.^{6,7}

In Fig. 2 the reference XRD spectrum of the HT-LiCoO₂ powder is displayed. The bar labels indicate the associated lattice plane reflections. In the same graph two typical diffraction spectra are plotted of annealed LiCoO₂ films deposited with rf sputtering and PLD, respectively. The 2θ values of all reflections observed match those in the reference spectrum with an accuracy of 0.04°. The two strong diffraction maxima at $2\theta = 33$ and 69° can be ascribed to the single crystalline silicon substrate and have been indicated as such. The peak located at 31.3° in the rf film spectrum is probably Co₃O₄ (220).

Not all diffraction peaks, characteristic of LiCoO₂, are detected and also different reflections are observed for rf films and PLD films. Due to the scanning geometry of the XRD equipment only the diffraction of the lattice planes oriented parallel to the substrate surface is observed (the detection angle is kept equal to the X-ray angle of incidence). A random unit cell orientation, as is common for powders, will result in a typical XRD powder pattern. The absence of specific diffraction intensities revealed that both samples exhibited strong preferential orientation. However, in the case of the rf film the (110) lattice plane reflection showed the highest intensity, while in case of the PLD film the (003) reflection was the major diffraction peak. Virtually no other LiCoO₂ diffraction maxima were detected. This indicates that the rf films have their (110) planes parallel to the substrate surface (c axis of the unit cell in plane of film). This orientation is perpendicular to that of the PLD films, which have their (001) planes parallel to the substrate surface (c axis of the unit cell normal to film surface).

The alignment of the unit cell toward the substrate is visualized in Fig. 3 for the PLD film and rf film, respectively. The reflecting lattice planes are indicated. Changing deposition conditions and film thickness had only an influence on the degree of crystal orientation. This is discussed in the following paragraphs.

Influence of annealing temperature.—In Fig. 4 the XRD spectra of 0.5 μ m rf films are shown as-deposited and after annealing treatment at 400 and at 600°C for 3 h (prolonged annealing). Small crystallites were already formed during deposition at 300°C (substrate temperature) as revealed by the broad, low intensity reflections at 2θ angles 36.5 and 65°. The XRD spectrum of the as-deposited PLD film (not shown here) had similar broad diffraction

Figure 1. Cross section of the LiCoO₂ unit cell along the hexagonal (110) plane. This representation visualizes the octahedral coordination of the cobalt (3a sites) and the lithium (3b sites) cations by oxygen (6c sites). Note the threefold rotation symmetry of the axes in the c direction.

peaks, but these were located around the positions of the (001) reflection. Annealing the rf film at 400°C for 3 h introduced additional broad reflections, ascribed to the (001) and (104) planes of the rock salt structure. Peak sharpening occurred after prolonged annealing at 600°C, revealing distinct diffraction peaks. The (110) reflection retained the highest intensity, followed by the (003). The presence of a small amount of Co₃O₄ is suggested by the occurrence of the (220) peak at 31.3° and a second (400) peak at 44.8°, which appears as the left shoulder of the (104) peak of LiCoO₂.

The existence of the HT-LiCoO₂ intercalation phase is generally confirmed by a distinct separation of the (110) and (018) reflections of a randomly oriented powder sample.⁸ The c/a ratio of the unit cell determines the position of these reflections. LT-LiCoO₂ is considered an ordered, cubic NaCl structure of the spinel type with overlapping (110) and (018) peaks [classified as the (440) reflection in space group $Fd\bar{3}m$]. An ideal close-packed lattice exhibits a c/a ratio of $2\sqrt{6} = 4.899$. In the case of the layered hexagonal structure of HT-LiCoO₂ the c/a ratio is reported to be (14.05/2.815=)

Figure 2. XRD spectra of typical submicrometer LiCoO_2 films deposited on silicon substrates with rf sputtering and pulsed laser deposition and annealed at 600°C for 30 min.

4.991⁹ which results in separation of the (110) and (018) reflections. The rf films only revealed the (110) reflection. The dominant nature of this reflection makes it difficult to discern whether peak splitting

Figure 3. Schematic drawing showing the LiCoO_2 unit cell orientation when deposited with rf sputtering (left) and with PLD (right).

Figure 4. XRD spectra of three $0.5\ \mu\text{m}$ rf films at different stages of preparation: as-deposited at 300°C and after annealing for 3 h in air at 400 and 600°C , respectively (spectra vertically displaced for clarity).

Figure 5. XRD texture analysis of the (110) diffraction of a $0.75\ \mu\text{m}$ rf film (annealed at 600°C , 30 min) visualized in a Wulff projection. Light shades of gray represent high intensity.

had not occurred yet or whether the (018) diffraction was out of the detection plane due to preferred orientation. Annealing at 900°C did not result in noticeable peak separation. The annealed PLD films showed neither the (110) nor the (018) reflection. However, the rf films annealed at 600°C for 3 h showed both the (003) and (110) diffraction peaks. This allowed calculation of the c/a ratio and a value of 4.894 was obtained, which suggests cubic symmetry and the absence of (110) and (018) peak splitting.

An X-ray texture analysis was performed to visualize the 3D orientation of the (110) planes on a $0.75\ \mu\text{m}$ rf film annealed only a short time at 600°C . The pole plot, shown in Fig. 5, indicates a fiber texture with a fixed (110) plane alignment. The major intensity is recorded at tilting angle $\varphi = 0^\circ$ and corresponds with the diffraction peak initially observed in the standard XRD spectrum (Fig. 2). An omega scan of this peak revealed a fwhm value of 6.25° , which indicates a sharp orientation distribution. Also at $\varphi = 60^\circ$ diffraction intensity is recorded at all rotation angles originating from the other two orientations of the (110) plane within the hexagonal unit cell. Consequently, the (104) planes show sharp diffraction intensity at $\varphi = 45^\circ$. Although the (003) peak diffraction, occurring at $\varphi = 90^\circ$, is technically undetectable, its presence was indicated by an intensity increase observed at $\varphi = 85^\circ$.

In this crystal alignment the required (018) diffraction is to be expected at $\varphi = 60^\circ$. The peak is indeed detected at $2\theta = 65.31^\circ$, well separated from the (110) reflection at $2\theta = 66.33^\circ$. The (018) reflection intensity is slightly less than that of the (110) planes ($\text{fwhm}_{(018),(110)} = 0.80$). Using the 2θ values the c/a ratio equals $(14.085/2.816) = 5.002$, which is in good agreement with the corresponding value of $(14.079/2.818) = 4.996$ calculated from the (110) and (104) diffraction angles, measured during the preceding texture analysis ($2\theta = 45.18^\circ$, recorded at $\varphi = 45^\circ$). Both ratios are close to the reported literature value of 4.991. Thus it is assumed that the phase transformation to HT- LiCoO_2 in thin films is possible and has occurred during annealing treatment at 600°C as has been reported for LiCoO_2 powders.

The oxygen background pressure during film deposition had little influence on the postanneal XRD spectrum. Tested p_{O_2} values

Figure 6. SEM micrographs showing the cross sections of rf films (60° tilt): $0.5\ \mu\text{m}$ LiCoO_2 on $0.15\ \mu\text{m}$ Al, as-deposited with rf sputtering (A) and after annealing at 600°C for 30 min (B), and $0.75\ \mu\text{m}$ LiCoO_2 on $0.15\ \mu\text{m}$ Al after annealing at 600°C in air for 30 min (C) and 3 h (D), respectively.

ranged between 1.10^{-7} and 5.10^{-7} mbar for rf sputtering and between 2.10^{-3} and 2.10^{-1} mbar for PLD. Some evolution of Co_3O_4 occurred during annealing at 600°C . At elevated temperatures volatile Li_2O is released and as a result LiCoO_2 is transformed. The process appeared to be accelerated by higher oxygen flows during annealing treatment. The (110) diffraction maximum of LiCoO_2 decreased with the increase of the Co_3O_4 reflections. Hence, annealing times should be kept as short as possible to prevent loss of active material. In other studies surplus Li_2O has often been incorporated in the target material to counterbalance this process.

Influence of annealing time.—The annealing time appeared to be of significant influence on the extent of the crystallization and the degree of preferential orientation of the LiCoO_2 film. The rf films annealed at 600°C for only 30 min, showed virtually only (110) diffraction (Fig. 2). The intensity and width of the reflections indicated that the annealing time had been sufficient to achieve complete crystallization. Samples, which endured annealing for longer times, developed a (003) diffraction peak, while the (110) reflection intensity diminished. Simultaneously the reflection intensities of the (101) and (104) planes increased slightly. Intensification of the (003) reflection intensity has also been reported by Wang *et al.*¹⁰ for LiCoO_2 thin films annealed in air at 700°C for 2 h.

Short exposure to the high annealing temperature proved essential to prevent deterioration of the initially strong preferential orientation of the polycrystalline film. Rapid thermal annealing (RTA)

experiments have been performed to reduce the annealing time to a minimum. Two $0.25\ \mu\text{m}$ rf films have been annealed at 550 and 600°C for only 1 min (ramp 10°C s^{-1}). The first film remained intact, while the latter was severely cracked. The XRD spectra of both rf films did not show any (00l) reflections and also lacked strong (110) preferential orientation. The second rf film also contained large amounts of Co_3O_4 . RTA under these conditions produced films with inferior integrity and phase purity compared to the regular short annealing procedure.

The cross section of an as-deposited rf film is shown in Fig. 6A. The morphology appeared amorphous. A columnar polycrystalline structure developed with annealing treatment at 600°C . This is visible on the micrographs of the rf film cross section in Fig. 6B and C, which also reveals the silicon substrate and aluminum current collector. Bates *et al.*¹¹ have recently observed similar LiCoO_2 film morphologies, but with a preferential (101) lattice orientation. No structural differences were observed between the rf films of 0.25, 0.50, and $0.75\ \mu\text{m}$ thickness.

Thin, hexagonal crystals were observed on the surface of the rf film when subjected to prolonged annealing treatment (Fig. 6D). Visualization using the backscattered electron mode of the SEM showed very low intensity between the bulk and the surface crystallites, which strongly suggests identical chemical composition. The exposure to high temperatures for a prolonged time has led to the outgrowth of crystals from the LiCoO_2 film. The crystals found on

Figure 7. TEM photograph of the cross section of an rf film annealed at 600°C for 30 min (A). Visible are the silicon substrate, the intermediate aluminum current collector (0.15 μm), Ti adhesive layer, and the LiCoO₂ film (0.75 μm). The electron diffraction pattern of the LiCoO₂ layer is shown below (B).

Figure 8. XRD spectra of 0.75 μm LiCoO₂ films deposited on different substrates (annealed at 600°C, 30 min): untreated silicon, HF-etched silicon and HF-etched silicon with 0.15 μm Al intermediate layer.

the surface lacked the preferential orientation as observed in the film, which corresponds to the previously discussed intensity increase of the (003) lattice plane reflection. In this situation the calculation of the c/a ratio using the $2\theta_{003}$ value could produce unreliable results.

The TEM cross section of the 0.75 μm LiCoO₂ rf film shows the columnar structure in detail (Fig. 7A). The dark area at the bottom is the silicon substrate and is covered with the intermediate aluminum layer and adhesive Ti coating. In Fig. 7B the recorded electron diffraction pattern of the LiCoO₂ film is shown. The large electron beam spot size guaranteed a statistically correct representation of the film texture. The reflections of the discussed (003), (104), and (110) lattice planes are labeled. The two intense (003) maxima indicate perpendicular orientation of the (00 l) planes toward the substrate surface. This was also derived from XRD spectra of rf films. With conventional XRD only those lattice plane reflections are detectable, which have their electron diffraction maximum on the imaginary line across the center of the pattern and parallel to the line of the substrate normal. This clearly illustrates why only the (110) lattice planes are observed with XRD analysis. Polycrystalline films with fully random orientation would exhibit circular electron diffraction patterns and thus powder-like XRD spectra.

Substrate influence.—The substrate has been reported to play an important role in determining the microstructure and surface morphology of the LiCoO₂ films.¹² To investigate this influence, rf films of 0.25, 0.50, and 0.75 μm thickness have been deposited on untreated silicon, on HF-etched silicon, and on silicon with an intermediate aluminum film (0.15 μm). The complete batch of nine samples was annealed *ex situ* at 600°C for 30 min.

In Fig. 8 three XRD spectra of annealed 0.75 μm rf films, deposited on various substrates, are shown. The LiCoO₂ film grown on the HF-etched silicon surface exhibited strong preferential (110) orientation. The application of the intermediate aluminum layer introduced some misalignment, which is reflected by the detectable diffraction of the (101) and (104) planes. The intensity of these reflections was larger for the rf film on untreated silicon, indicating increased randomness of crystal orientation. The substrate and its pretreatment indeed influenced the degree of texture.

The rf films have been cleaved for SEM observation of the layer cross section. The SEM analysis revealed superior adhesion of the LiCoO₂ film on the intermediate aluminum layer. On all photographs the jagged edge of the LiCoO₂ film followed the fracture line of the silicon accurately and never showed any sign of peeling, as observed for other stack configurations. XRD analysis also provided evidence for the strong interaction between the LiCoO₂ film and the aluminum film. The observed preferential (111) orientation of the Al

Figure 9. Three-dimensional AFM representation of the surface of the rf film (left) and the PLD film (right) after annealing at 600°C for 30 min.

crystallites switched to (220) with annealing treatment. This orientation change was not observed in the absence of the LiCoO_2 film. The extreme decrease of the (111) aluminum reflection at 38.5° is recognizable in Fig. 4. The rise of the Al (220) reflection (located at 65.1°) is less apparent in this figure due to its lower intensity and the dominance of the (110) reflection of LiCoO_2 . The presence of LiCoO_2 apparently determined the final crystal orientation of the aluminum layer, while the boundary between the aluminum and the transition metal oxide remained sharp and straight and appeared unaffected on the TEM photograph.

To examine the consistency of the preferred lattice orientation of the PLD and rf films toward each other, a PLD film was grown on an rf-sputtered seed layer of $0.1 \mu\text{m}$ LiCoO_2 (annealed at 600°C, 30 min). As a reference, PLD was simultaneously performed on a blank silicon substrate. This reference sample revealed the typical PLD film diffraction pattern, indicating (00 l) lattice plane orientation. The PLD film deposited on the seed layer, which exhibited only the

(110) reflection before PLD, showed distinct (006) and (0012) reflections, but the (003) and (009) reflections were completely absent. This result indicates that the film structure is not entirely determined by the deposition technique. The distinctive diffraction pattern can be explained by assuming complete cationic disorder.¹³ A random distribution of the lithium and cobalt atoms would lead to a structure similar to that of NaCl. Hence, the (003) and (009) reflections become extinct.

Atomic force microscopy (AFM).—Figure 9 shows the three-dimensional representation of the surface of the rf film and the PLD film. Both samples consisted of films of equal thickness and comparable history (annealed at 600°C for 30 min). The rf film exhibited coarser grains and increased surface roughness compared to the PLD film. The LiCoO_2 lattice growth during deposition and annealing treatment is not isotropic. Apparently the growth rate of both the (110) oriented rf film, whose c axis was parallel to the film surface and the (003) oriented PLD film with its c axis normal to the film surface, was larger along the a axis. This is in agreement with the observed outgrowth of crystals on the surface of rf films during prolonged annealing at elevated temperatures.

RBS.—The rf film annealed at 600°C for 30 min was also characterized with Rutherford backscattering (RBS) analysis. The RBS spectrum recorded in the center of the rf film is shown in Fig. 10. The oxygen-cobalt ratio was determined to be a few percent above two. The measurements also confirmed a constant composition profile and constant film thickness across the full sample width. Small oscillations in the Co recoil spectrum suggest that the oxygen content is higher near the surface of the film. This could be explained by the presence of some Li_2O .

The recoil intensity on the low energy side of the Co spectrum decreases gradually, indicating a surface roughness of the substrate or a reaction zone of approximately $0.13 \mu\text{m}$ thickness. Some inter-layer diffusion of cobalt ions may have occurred at 600°C. However, the TEM photographs revealed that the substrate- LiCoO_2 interface remains distinct upon annealing and judging by the AFM results, surface roughness is most likely to be the major cause of the fading recoil spectrum.

Figure 10. RBS spectrum of $0.75 \mu\text{m}$ rf-sputtered LiCoO_2 film on silicon substrate annealed at 600°C for 30 min.

Conclusions

The preparation of preferentially oriented, submicrometer LiCoO_2 films has been achieved. The deposition technique largely determined the LiCoO_2 unit cell alignment with the substrate and, thus, the preferential orientation of the film. RF and PLD films exhibited (110) and (003) lattice planes parallel to the substrate surface, respectively. Deposition at 300°C on pre-etched silicon substrates and subsequent short annealing treatment at 600°C provided uniform film texture. Prolonged annealing treatment resulted in loss of LiCoO_2 and degradation of the preferential orientation.

This research has shown that LiCoO_2 films with well-defined geometry and structure can be prepared using materials common to the integrated circuit industry. A material interaction at the interfaces between the layers of the stack has been observed, but this is considered beneficial since it contributed to the adhesion strength of the LiCoO_2 film to the substrate. Thus these films are suitable for fundamental research on electrochemical lithium intercalation and have a prospect for application in microbatteries. The favorable outward orientation of the lithium diffusion plane, which is only the case for the (110) oriented rf films and the high surface area of these films could lead to excellent intercalation electrode characteristics. A full report on the electrochemical properties will follow in a future publication.

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