

Structural, compositional and electrochemical properties of Aluminium-Silicon-Chromium alloy thin film as anode for Lithium thin film battery

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Abstract: In recent years, many new materials have been investigated in order to meet the need of high energy density for thin film batteries. Silicon based anode materials are attracting wide attention because of the highest theoretical capacity. By using DC magnetron sputtering method Aluminium film was deposited on ceramic substrate which acts as a current collector. Nanocrystalline film of Aluminium-Silicon-Chromium(Al-Si-Cr) alloy was deposited on aluminum film by using same sputtering method. High purity Aluminium-Silicon-Chromium metal alloy sputtering target was used for the film deposition. For comparison of anode cycling performance, pure Silicon thin films were also prepared by using same sputtering method. Al-Si-Cr films were analysed by XRD, EDAX, AFM and SEM . The crystallite size was determined by FWHM of XRD peaks. Particle size and microstructure of the film have been studied by SEM and AFM. The Al-Si-Cr thin film composition was analysed by EDAX. Composition ratio between Aluminium Silicon and Chromium obtained by EDAX is 2:3:5. Electrochemical properties of the films were analyzed by preparing lithium battery cell. Lithium insertion and excretion was performed by Cyclic Voltametry.

Effect of cycling on structure stability of Al-Si-Cr anode film was studied by SEM analysis.

Keywords: anode , Al-Si-Cr alloy, thin film , battery, lithium , magnetron sputtering ,

I. Introduction

In last decade, focused research has been conducted on thin-film micro batteries as a power source for Microsystems [1-3]. Subsequently, there have been considerable efforts in finding new materials to replace the existing lithium battery anode [4-10].

It is already known that as a naturally abundant element, Si has the highest theoretical specific capacity among all existing anodes, which can reach 4200 mAh/g in the form of $\text{Li}_{4.4}\text{Si}$ [11–16]. Unfortunately, its potential in broad commercial applications has been hindered by severe capacity fading and loss of electrical contact caused by huge volume change, structural crumbling and cracking during repeated charging/discharging, especially at high currents .It could be overcome by using a multiple-layer thin comprising a silicon (Si) layer and a transition metal (M) layer[17-18]. Where metal (M) is incompatible with Lithium. This leads to the question whether the metal (M) layer can act as a diffusion barrier against Li penetration during Li insertion/extraction reactions of the multilayer film electrode. Another approach for solving the problem of silicon capacity fading is using ternary alloy materials as anodes. Some researchers have reported their work of ternary system with Al-Si-Mn [19-20]. Consequently, these anodes presented poor cycle performances. For example, the first discharge specific capacity of the $\text{Al}_{59}\text{Si}_{40}\text{Mn}_1$ anodes could achieve 1803mA-h/g, but declined to 636 mAh/g in the next cycle. As a result, a low specific capacity of 125 mAh/g was shown after 10 cycles. Hence a substitution for the third inert component in place of Mn might be an effective method to obtain better cycle performances. According to the binary alloy phase diagrams [21], the solubility of Li in Cr is less than that in Mn. In this paper the DC magnetron sputtered film of Al-Si-Cr alloy is investigated as anode material for lithium-ion battery.

II. Experimental details

All the films were deposited using DC magnetron sputtering technique. The target used (metal alloy to be deposited) was with 20 Wt % Aluminium, 30 Wt % Silicon and 50 Wt % Chromium make M/s Heraeus Germany. {Purity of each individual metal was 99.99 % }. The pure Aluminum target {purity 99.99 % } was from M/s Kistar, Korea. The substrate used was alumina containing ceramic plate supplied by M/s Murata, Japan. The surface roughness of ceramic plate was 0.180 μm . The sputtering equipment used was of Balzer make. This sputtering technique uses an inert gas which is ionised under application of high voltage under vacuum. Argon gas is selected, as argon ions are heavy enough to knock metal atoms out of target. Ions are attracted by target which has negative voltage and are accelerated under influence of magnet fitted above target. For Al-Si-Cr thin

film deposition extensive trials were conducted with varying sputtering parameters. Optimum parameters were derived to get best possible and stable film morphology. Following optimized parameters were employed for deposition of Al-Si-Cr films.

Argon Gas Purity- 99.99 % ,Argon Gas pressure – 5mTorr ,Sputtering Power– 150 watt , Sputter deposition time – 60 min , Extent of Vacuum in sputtering chamber- 3×10^{-6} bar.No post heat treatment was given to films.

For comparison of anode cycling performance pure Silicon thin films were also prepared by using same sputtering method.Pure Silicon sputtering target{purity 99.99% } was also supplied by M/s Heraus,Germany

The composition of deposited Al-Si-Cr and aluminum films was characterized by energy dispersive X-ray analysis (EDAX) to ensure identical composition of the starting target and the deposited films. The surface microstructure was determined by SEM and AFM. The XRD experiments were carried out with $\text{CuK}\alpha$ radiation. Cyclicvoltammetry (CV) properties were measured with the cell which was composed of a metal Lithium foil as a counter electrode. 1M LiPF_6 in 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was used as Electrolyte. Cells were fabricated to test the electrochemical properties of thin-film electrodes. The cells were assembled in an argon filled glove-box. AFM and SEM images of Al-Si-Cr and Aluminum films were taken before and after cycling.

III. Results and discussion

An X-ray diffraction pattern of Al-Si-Cr thin film is shown in Figure 1.It demonstrates thin films with crystalline aluminum peaks according to JCPDS 04-0787[22]. Peaks for the (111), (200), and (220) are clearly observed in the XRD plots below. Note that a broad peak accompanied by stronger, sharper peaks around 65 degrees is generated due to the silicon. Thin films deposited on ceramic and aluminum nitride substrate had a dominant (111) orientation,. It was expected for sputtered aluminum-silicon-chromium films to be highly crystalline in this respect. From the width of the diffraction peaks, the average grain size was calculated according to the Scherrer equation (crystallite size $D = 0.9\lambda = B\text{Cos}\theta$). The estimated average crystallite size for the Al-Si-Cr alloy deposited thin film is about 45 nm. Composition ratio between Aluminium ,Silicon and Chromium was obtained by EDAX as shown in Figure 2. The EDAX spectrum shows that elemental composition of deposited Al-Si-Cr film is in good agreement with composition of starting Al-Si-Cr metal alloy target composition. The AFM image of the Al-Si-Cr thin film is shown in Figure 3.It shows that root mean square roughness R_q is 23.2 nm and indicates that the deposited film is very smooth and uniform. SEM image in Figure 4 also confirms that Al-Si-Cr is deposited as a uniform matrix.

The Li insertion/removal into the film was done by CyclicVoltametry. Figure 5 shows CV voltamogram .From the CV results, it can be seen that Li insertion reaction occurred mostly at low potential below 0.2V. The peaks obtained are attributed to the potential dependent formation and disappearance of Li-Si alloys of different compositions given by Wen and Huggins [23]. The difference in the potential for each peak can be ascribed to the kinetic effect involved in the CV measurement [24]. The peaks observed on the second cycle were compared with the first cycle in that two cathodic/anodic peaks decrease significantly at 0.2/0.3V and an anodic peak at 0.5V shifts toward a higher potential.The irreversible reaction of the first cycle seems to be associated with the formation of a solid electrolyte interface (SEI)layer or dangling bond which is related to phase transformation [25]. Therefore, the significant reduction of peak at 0.2V indicated that the irreversible reaction was suppressed by maintaining the equilibrium state in the second cycle. The potential shift of about 0.1V from 0.5 to 0.6V also indicates increased kinetic polarization and internal resistance.

The discharge capacity of Al-Si-Cr anode as a function of the number of cycles is shown in Figure 6. It is observed that Al-Si-Cr films gradually degraded with cycling. However, Al-Si-Cr thin film anode showed higher discharge capacity and capacity retention as compared to the pure silicon thin film anode. Pure Silicon thin film anode cycling data was comparable with data reported in other literature [26-28].Capacity retention after 50 number of cycles for Al-Si-Cr anode was 77 % and that for pure Silicon anode was 52 %. SEM analysis was performed on Al-Si-Cr anode film after cycling. Figure 7 shows the SEM micrographs of Al-Si-Cr anode film before and after cycling. It clearly shows that due to cycling stress film structure is changed.The sharp grain boundaries collapsed and got merged in each other suggesting starting of loss adhesion between substrate and anode film[29].

IV. Figures and Table

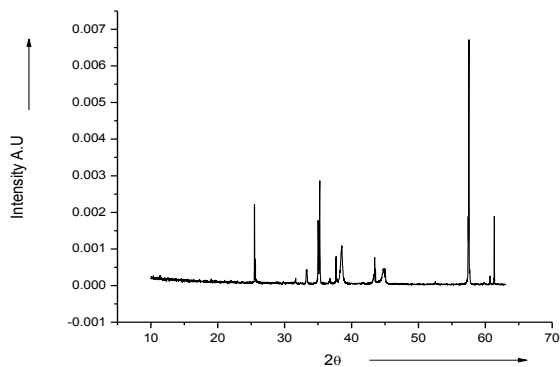
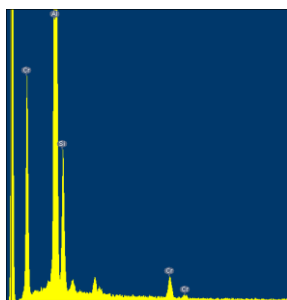


Fig1:XRD plot of Al-Si-Cr thin film



Element	Weight%
O K	37.44
Al K	12.75
Si K	17.90
Cr K	31.91
Total	100.00

Fig2:EDAX spectrum of Al-Si-Cr thin film on ceramic substrate

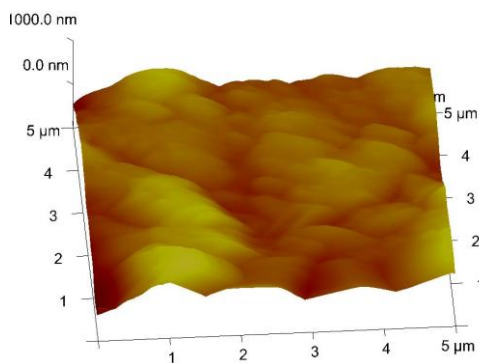


Fig3:AFM image of Al-Si-Cr thin film

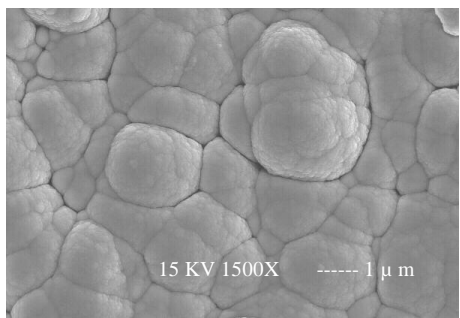


Fig 4: SEM micrograph of Al-Si-Cr thin film

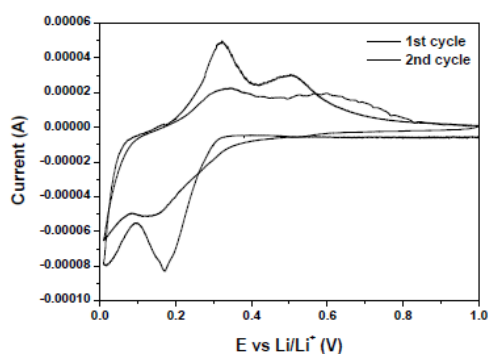


Fig. 5: The cyclic voltammogram of Al-Si-Cr thin film

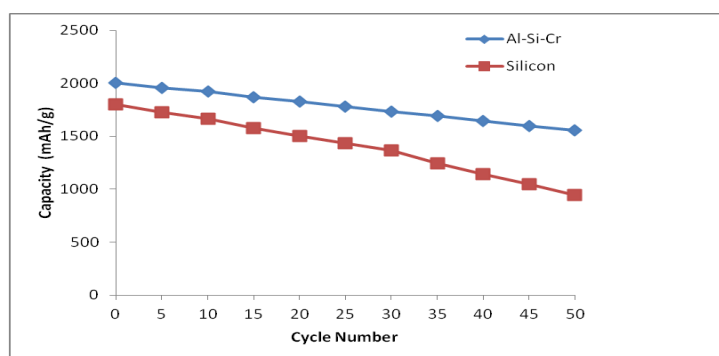


Fig 6: Cycling performance of Al-Si-Cr and pure Silicon anodes

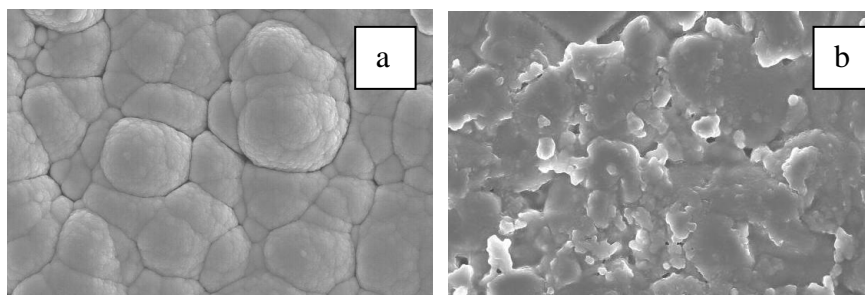


Fig 7: SEM micrographs of before and after cycling of Al-Si-Cr anode
a. Before cycling b. After cycling

V. Conclusions

Stable thin films of pure Aluminum and Al-Si-Cr metal alloy were successfully prepared using DC magnetron sputtering. XRD studies confirmed that the grain size of Al-Si-Cr film is in the nanometer range. The electrochemical properties and micro structural stability of a Al-Si-Cr film have been investigated. Cyclic voltammetry studies have confirmed that Al-Si-Cr thin films are active towards Lithium. Capacity vs. cycle study suggests that Al-Si-Cr has significant higher performance in terms of initial discharge capacity and capacity retention. We believe that further optimization of substrate surface morphology will lead to better adhesion of anode leading to improvements in cycling performance.

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