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Fabrication and Photoelectrochemical Properties of Al-substituted α-Fe_2O_3 Photoelectrodes by Pulsed Laser Deposition

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Abstract

Al-substituted α-Fe_2O_3 ($Fe_{2-x}Al_xO_3$: 0.0<x<1.0) thin films were grown on α-Al_2O_3 (110) substrates with a Ta-doped SnO_2 electrode layer using pulsed laser deposition for solar energy harvesting. Highly oriented epitaxial films with pure corundum structures were successfully fabricated over the entire compositional range. The photoelectrochemical performance was improved in the slightly Al-substituted film. We found that the optimum Al content lies at around x = 0.25, where the photocurrent is significantly enhanced over a wavelength range of 300–700 nm.

1. Introduction

Photoelectrochemical (PEC) water splitting is a promising method to convert solar energy into fuel energy directly. Among the various materials for the photoelectrode, hematite (α-Fe_2O_3) is regarded as a candidate for its suitable band gap, stability and abundance [1]. However, the poor carrier transport properties and the mismatch between the band edge positions and the water reduction and oxidation potentials, have limited the PEC performance of hematite. The effect of doping third elements such as Si and Ti in hematite has been studied yet, which can increase the transport properties thus enhance the PEC performance [2]. In previous study, we induced Rh as substituted element for Fe [3]and we found band gap narrowed. This time we use the abundance element Al as substituted element. Although the doping effect of Al in hematite has already been studied in previous study [4], for the difficulty of being a solid solution in bulk, the photoelectrochemical properties of well Al-substituted hematite films were not been studied yet. In this research, we fabricated Al-substituted hematite thin films successfully by pulsed laser deposition, and their photoelectrochemical properties was investigated.

2. Experiments and Results

Fabrication of thin films

$Fe_{2-x}Al_xO_3$ films are fabricated by pulsed laser deposition (PLD), at 700 ℃ under oxygen pressure P_O=0.1 Pa. For the PEC measurement, Ta-doped SnO_2 (TTO) was deposited on the α-Al_2O_3 (110) substrate at 800 ℃ under oxygen pressure P_O=0.1 Pa, as a bottom electrode prior to the growth of $Fe_{2-x}Al_xO_3$ films. The target for PLD was prepared from α-Fe_2O_3 and α-Al_2O_3 powders via a standard solid-state reaction.

The structure properties are studied by X-ray diffraction (XRD). Fig. 1 shows the XRD patterns of $Fe_{2-x}Al_xO_3$ thin films. The lattice constant a calculated from the (110) peaks decreases linearly with increasing x (see inset of Fig.1). These data obeyed Vegard's law, indicating that Fe was appropriately substituted by Al.

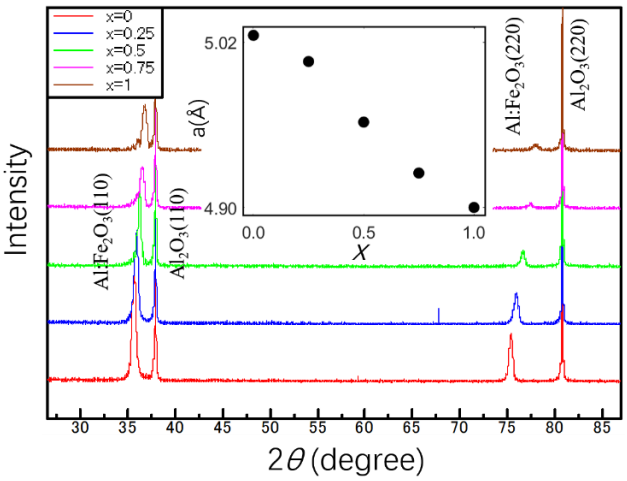
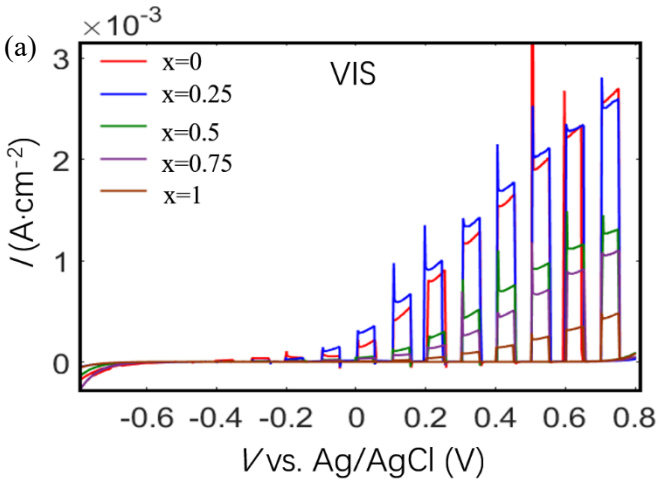


Fig. 1 XRD patterns of $Fe_{2-x}Al_xO_3$ films grown on Al_2O_3 substrate with x values of 0, 0.25, 0.5, 0.75 and 1. The inset shows the compositional dependence of the lattice parameter a.

Photoelectrochemical measurement

The photoelectrochemical properties were measured in a



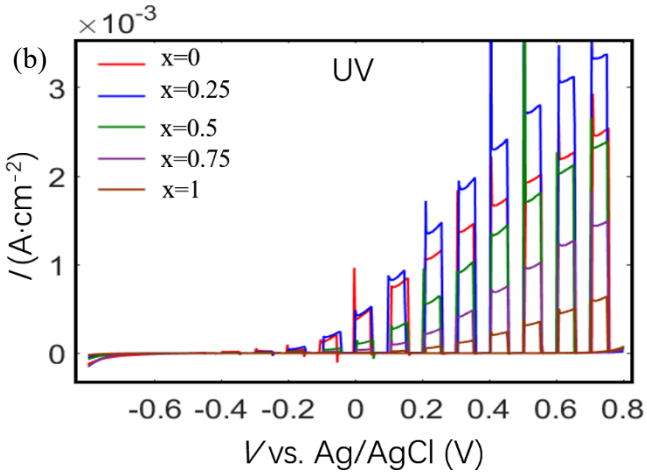


Fig. 2 Chopped *I-V* curves under illumination with (a) vis light (λ=400-700 nm) and (b) UV light (λ=300-400 nm) for $Fe_{2-x}Al_xO_3$ photoelectrodes.

three configuration with Pt counter electrode, 3M NaCl saturated Ag/AgCl reference electrode and the $Fe_{2-x}Al_xO_3$ samples as working electrode. A 100W Xe lamp was used as a light source along with a quartz electrolytic cell filled with 1M NaOH solution. Fig.2 shows the photo induced current-voltage curves measured in this condition. Under vis. illumination, the photocurrent was enhanced slightly by Al substitution with x=0.25, on the other hand, samples with large x seem to show poor photoelectrochemical properties. However, under UV illumination, the enhancement of photocurrent in sample with x=0.25 to hematite was observed clearly. And the photocurrent of sample with x=0.5 also shows a more positive change from vis. to UV illumination at 0.7 V, compared to pure hematite, which may attributed to bandgap broadening by Al substitution.

Mott-Schottky plot

Mott-Schottky analysis was carried out at an AC frequency of 1 kHz and amplitude 10mV in darkness. Fig.3 shows the result.

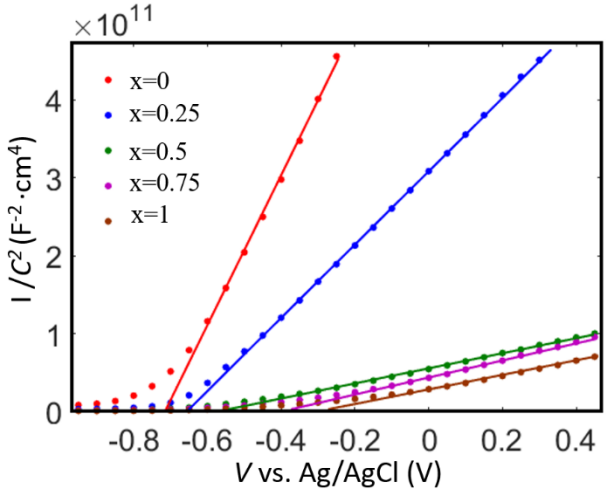


Fig.3 Mott-Schottky plot of $Fe_{2-x}Al_xO_3$/TTO. Electrolyte solution: 1 M NaOH.

The flat band potential E_{fb} and the donor carrier density N_D were calculated from the following equation: [5]

$$\frac{1}{c^2} = \frac{2}{e\varepsilon\varepsilon_0 N_D}\left(V - E_{fb} - \frac{k_B T}{e}\right) \qquad (1)$$

Table I summaries the result of the calculation. We found that flat band potential shifts linearly with x increasing, suggesting that the conduction band edge was changed by the Al-substitution. The donor carrier densities ranged from 7.6×10^{19} to 7.8×10^{19}, which is consistent with the order in reference [5]. Compared to pure hematite, an increasing by 2-fold (x=0.25) to almost one order (x=0.5, 0.75, 1) in donor carrier densities was found.

Table I Flat band potential and donor carrier density of $Fe_{2-x}Al_xO_3$

Samples	E_{fb} (V)	N_D (cm^{-3})
x=0	-0.71	7.6×10^{19}
x=0.25	-0.66	1.6×10^{20}
x=0.5	-0.54	7.4×10^{20}
x=0.75	-0.38	6.5×10^{20}
x=1	-0.28	7.8×10^{20}

3. Conclusion

Al-substituted hematite thin films were successfully fabricated by PLD and there photoelectrochemical properties were investigated. With Al-substitution, hematite photoelectrodes indicate larger donor carrier densities, and the flat band potential were changed. The sample with x=0.25 shows the better photochemical performance than pure hematite.

References

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