Direct Electrodeposition of 1.46 eV Bandgap Silver(I) Oxide Semiconductor Films by Electrogenerated Acid

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Photovoltaic cells (PVs) have been attracting increasing attention as an effective and sustainable energy source. The energy conversion efficiency of PVs depends closely on the bandgap energy of a light absorption layer integrated into the cell. In terms of an ideal bandgap energy of 1.4–1.5 eV based on a theoretical calculation,[1] CdTe[2] and Cu-$(In_{1-x}Ga_x)Se_2$[3] have been developed as a light absorption layer that is superior to Si used conventionally. However, the compounds contain toxic elements.

Silver(I) oxide (Ag_2O), a p-type semiconducting oxide, has been used mainly in the thin film sensor[4] and as a cathode in the zinc-silver oxide battery.[5] The bandgap of Ag_2O, which has the same crystallographic structure as Cu_2O, i.e., cubic cuprite, has been determined to be 1.3 ± 0.3 eV experimentally.[6] This indicates that Ag_2O is potentially suitable for an ideal light absorption layer not containing toxic elements. Fulfilling the significance of PVs requires obviously a low temperature, large-scale, and lower-cost synthetic method.

Soft solution processes including electrodeposition from aqueous solution are a promising technique that offers the direct synthesis of metal oxides satisfying the above-mentioned requirements.[7] Various oxide semiconductors such as ZnO,[8] CeO_2,[9] Cu_2O,[10] and TiO_2[11] have been electrodeposited directly on substrates from aqueous solution.

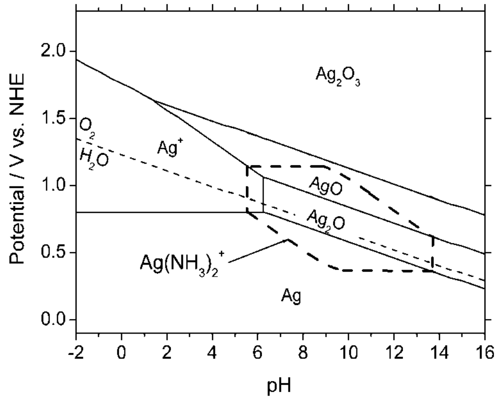

Figure 1. Potential−pH diagram of a Ag-H_2O (solid line) and Ag-NH_3-H_2O (dashed line) systems at 25 °C, where the activity of dissolved species is 1.

Switzer et al.[12] have reported the electrodeposition of AgO films using an anodic oxidation strategy from an acidic aqueous solution containing silver acetate and sodium acetate. As shown in the potential−pH diagram[13] of a Ag-H_2O system (Figure 1, solid line), the thermodynamically stable region of AgO lies at a potential nobler than that of Ag_2O and extends to the acidic region, allowing the anodic electrodeposition

$$Ag^+ + H_2O \rightarrow AgO + 2H^+ + 2e^- \qquad (1)$$

In contrast, cathodic polarization causes easily the deposition of Ag metal at a broad range of pH

$$Ag^+ + e^- \rightarrow Ag \qquad (2)$$

The reduction of molecular oxygen and nitrate ions, which generates hydroxide ions, has been used for depositing high-quality oxides such as ZnO from aqueous solution and the reaction schemes are as described below (reactions 3−5). Because the reduction of Ag^+ (2) is preferred to that of dissolved oxygen and nitrate ions (reactions 3 and 4), the formation of Ag_2O by the cathodically electrogenerated base is quite difficult and different from a case of ZnO.[8]

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (3)$$

$$NO_3 + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \qquad (4)$$

$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O \qquad (5)$$

In the present study, the direct electrodeposition of Ag_2O with a bandgap energy of 1.46 eV was achieved for the first

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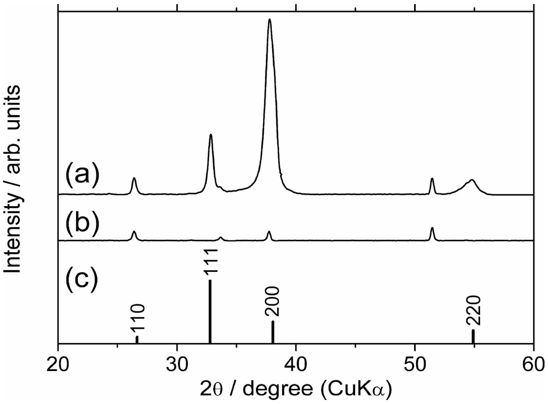

Figure 2. XRD patterns of (a) a Ag_2O film electrodeposited from an ammoniacal electrolyte at a current density of 10.0 mA cm^{-2} and (b) a F:SnO_2-coated glass substrate. (c) JCPDS data (41–1104) for Ag_2O.

time using a novel pathway termed "oxides synthesis induced by electrogenerated acid". We conducted the anodic electrolysis of an alkaline aqueous solution (pH 12)[14] containing 0.20 M (M = mol dm^{-3}) silver(I) nitrate and 0.73 M ammonia using an H-type separated cell (see the Supporting Information).[15] The thermodynamically stable region of dissolving silver(I) species is expanded to the alkaline region by forming ammonia silver complex ion, $[Ag(NH_3)_2]^+$, as shown in Figure 1(dashed line).[16] An anodic current density of 10.0 mA cm^{-2} was applied galvanostatically to a conductive glass substrate (F:SnO_2) in the aqueous solution at 25 °C using a Pt wire and Pt plate as a quasireference[17] and counter electrode, respectively. Characterization of deposits obtained was performed by X-ray diffraction (XRD, Rigaku RINT2500) measurement, field-emission scanning electron microscope (FE-SEM, JEOL6700F) observation, and X-ray photoelectron spectroscopy (XPS, ULVAC-PHI57-00MC) analysis. Bandgap energy and electrical properties were evaluated with a UV–vis spectrophotometer (Shimadzu UV3150) and a Hall effect measuring system (Toyo Technica Resitest 8310).

When a constant current density of 10.0 mA cm^{-2} was applied anodically to a F:SnO_2-coated glass substrate, the evolution of O_2 gas was observed accompanied by the formation of dark-gray deposit on the substrate. During the electrolysis such phenomena occurred continuously, and the deposit obtained by passing quantity of electric charge of 5 C cm^{-2} had a homogeneous and smooth appearance. An XRD pattern of the resultant deposit is presented in Figure 2. All diffraction peaks could be assigned to either F:SnO_2 or Ag_2O with a cubic cuprite structure (JCPDS 41–1104). A comparison with the JCPDS data indicates that the electrodeposited Ag_2O has a ⟨100⟩-preferred growth orientation. The lattice constant of the Ag_2O was calculated to be 4.73 Å from the XRD pattern, which is consistent with the JCPDS data, 4.72 Å.

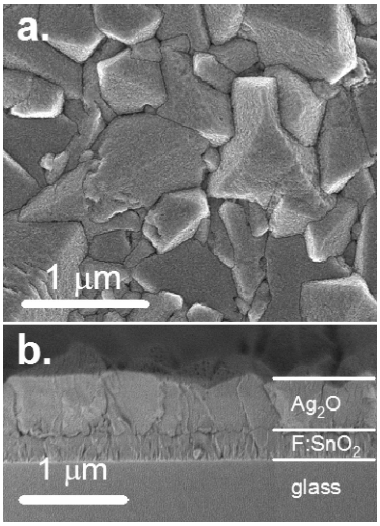

Figure 3. (a) Top-view and (b) cross-sectional FE-SEM images of Ag_2O electrodeposited from an ammoniacal electrolyte at a current density of 10.0 mA cm^{-2}.

Table 1. Binding Energy for Ag(3d) and O(1s) Photoelectrons for Ag_2O Electrodeposited from an Ammoniacal Electrolyte at a Current Density of 10.0 mA cm^{-2}

	binding energy (eV)[a]	
compd	Ag($3d_{5/2}$)	O(1s)
electrodeposited Ag_2O	368.0	529.4
Ag[b]	368.3	
Ag_2O[b]	367.9	529.4
AgO[b]	367.5	528.7 531.6

[a] Binding energies measured were corrected for adventurous carbon so (C1s) = 284.5 eV. XPS analysis was performed with monochromated Al Kα radiation at a pressure of ~1.6×10^{-8} Pa. [b] Literature values cited in the paper by Murray et al.[18]

Surface and cross-sectional FE-SEM images of the Ag_2O electrodeposited by passing quantity of electric charge of 5 C cm^{-2} are shown in Figure 3. The surface is well-faceted and continuous over the entire substrate. Four-sided pyramidal grains seen in the image corresponds to the ⟨100⟩-orientated Ag_2O. The cross-sectional image reveals the growth of ~0.5 μm thick Ag_2O without grain boundaries parallel to the substrate plane.

Electronic states of the Ag_2O film were examined on Ag 3d and O 1s by XPS analysis (Table 1, and see the Supporting Information). Ag $3d_{5/2}$ and O $1s$ peaks were observed at binding energies of 368.0 and 529.4 eV, respectively. These values agree well with those for Ag_2O in the literature.[18] The results of the XRD pattern and XPS analysis show that the deposit is polycrystalline single-phase Ag_2O.

A plot of $(\alpha E)^2$ vs E for a 1.0 μm thick Ag_2O film, where α and E are the optical absorption coefficient and photon energy, respectively, is shown in Figure 4, representing a linear relationship at photon energies above the absorption edge. This indicates that the electrodeposited Ag_2O is a direct semiconductor.[19] The bandgap energy was estimated to be 1.46 eV by extrapolating a linear part of the plots to $(\alpha E)^2$

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(14) The pH was adjusted by adding a NaOH solution.

(15) *Caution: It is possible that the reaction of high concentration silver nitrate and ammonia, or electrolysis solution (including diluted solutions) left for a long time, might give fulminating silver (explosive nature). The electrolysis solution must be inactivated with chloride salts such as NaCl after the experiments without delay.*

(16) For the calculation, a complex formation constant of $10^{7.31}$ was used.

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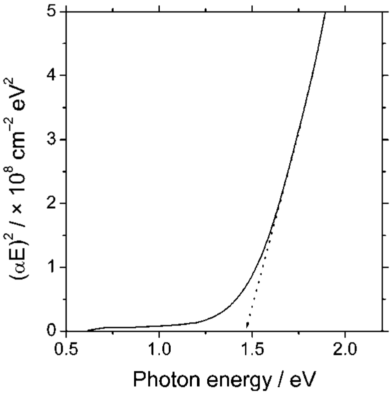

Figure 4. Dependence of $(\alpha E)^2$ on photon energy for a 1 μm thick Ag_2O film electrodeposited from an ammoniacal electrolyte at a current density of 10.0 mA cm^{-2}.

= 0, which is an ideal value for a light absorption layer in PVs. An optical-absorption coefficient was 1.54×10^4 cm^{-1} at a wavelength of 500 nm.

Electrical properties for the electrodeposited Ag_2O film were evaluated with a van der Pauw method using the Hall measuring system. Resistivity, carrier density, and mobility were 5.7×10^2 Ω cm, 1.0×10^{16} cm^{-3}, and 1.1 cm^2 V^{-1} s^{-1}, respectively.

The present anodic electrodeposition of Ag_2O from the ammoniacal electrolyte can be explained by the following deposition mechanism:

(i) in the bulk of solution

$$Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ \qquad (6)$$

(ii) in the vicinity of an electrode

$$H_2O \rightarrow 2H^+ + 1/2O_2 + 2e^- \qquad (7)$$

$$[Ag(NH_3)_2]^+ + 2H^+ \rightarrow Ag^+ + 2NH_4 \qquad (8)$$

$$2Ag^+ + 2OH^- \rightarrow Ag_2O + H_2O \qquad (9)$$

$$NH_3 + H_2O \rightarrow OH^- + NH_4 \qquad (10)$$

Complexation of a silver(I) ion with ammonia (reaction 6) allows an alkaline aqueous solution (pH 12) containing dissolving silver(I) species without precipitation as shown in Figure 1 (dashed line). During a galvanostatic electrolysis at 10 mA cm^{-2}, a F:SnO_2 electrode kept a constant potential (see the Supporting Information) and the evolution of oxygen gas was observed, suggesting that the electrolysis of water (reaction 7) occurred continuously. A part of the generated protons should react with the ammonia silver(I) complex to yield transient free silver ions in the vicinity of the substrate surface (reaction 8). And the free silver ion is then hydrolyzed to precipitate Ag_2O onto the substrate (reaction 9) because both the environmental pH and electrode potential, i.e., the potential of anodic water electrolysis (reaction 7), are consistent with the thermodynamically stable region of Ag_2O (Figure 1). The local pH decrease caused by reactions 7 and 9 can be compensated by excess NH_3 (ca. 0.3 M), keeping the pH above 11 (reaction 10). Although it is possible that the deposition and redissolution of Ag_2O to form the complex is competitive according to the potential−pH diagram, continuous growth was observed. The similar mechanism based on the water oxidation, followed by the hydrolysis of silver ions, has been proposed for the synthesis of dispersed Ag_2O colloids from a silver electrode.[18] The present deposition mechanism based on "the decomposition of a complex by electrogenerated protons" is quite novel, offering a new electrochemical strategy to give metal oxide films.

In summary, we have discovered a direct electrodeposition method of Ag_2O films for the first time using a new strategy termed "oxides synthesis induced by electrogenerated acid". The Ag_2O film with bandgap energy of 1.46 eV and resistivity of 5.7×10^2 Ω cm was obtained at 10.0 mA cm^{-2}, which is suited to a light absorption layer in photovoltaic cells.

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Supporting Information Available: Figure S1, experimental setup; Figure S2, XPS spectra for a Ag_2O film; Figure S3, deposition potential curve for the Ag_2O electrodeposition (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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