3. The basic action of an anion is similar to that of an addition agent.
4. The morphologies from simple acidic copper solutions at low C.D. and thickness are of a similar overall shape, the differences are more remarkable at increasing C.D.'s and thicknesses and in deposits from complex solutions. No specific evidence of an anion effect is observed.

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Cathodic Deposition of Amorphous Silicon from Tetraethylorthosilicate in Organic Solvents

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ABSTRACT

A blue thin film of amorphous silicon has been deposited on a nickel cathode by the electrolysis of a solution of tetraethylorthosilicate in acetic acid. The maximum thickness of the film obtained was about 0.5 μm. The deposit was confirmed to be amorphous silicon by *IR* reflection spectra, RHEED, and nondispersive x-ray analysis in the scanning electron microscope.

Amorphous silicon containing hydrogen, a-Si, is a promising material for the manufacture of low-cost large area solar cells with medium efficiency. Amorphous materials not containing hydrogen appear to have large concentrations of dangling bonds, producing levels in the forbidden gap which give the material a high resistance and make a change of the semiconducting properties by doping virtually impossible (1). In materials made in a glow discharge in silane, however, these bonds are saturated by hydrogen, the levels disappear, and doping to n- and p-type with appreciable conductivity becomes possible (2, 3). Conversion efficiencies as high as 6% have been measured in sunlight (4). The theoretical limit for the efficiency of a thin film a-Si solar cell is estimated to be around 15% (5).

Materials made in different ways have different properties. Amounts of H larger than required to saturate the dangling bonds lead to $(SiH)_n$ polymer formation with less favorable electrical properties. It is, therefore, important to regulate the hydrogen

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Key words: amorphous silicon, electrodeposition, tetraethylorthosilicate, nonaqueous electrolyte.

content of the material. Electrodeposition as a method of preparation is attractive for various reasons: It is easy to regulate the hydrogen content of a-Si; it does not involve vacuum equipment or furnaces and is therefore convenient; doped material can be made by adding compounds of the dopant to the electrolyte. It is therefore attractive to apply this method to amorphous silicon. However, the strong affinity of silicon for oxygen makes electrodeposition from aqueous electrolytes impossible. The use of organic solvents removes this difficulty.

Amorphous germanium (together with hydrogen) was plated from ethylene glycol (6). There are a few indications in the literature for a-Si electrodeposition. Warren reported electrodeposition of Si on Hg from a solution of SiF_4 in alcohol (7). Zyazev and Ezrielev described the cathodic deposition of Si on Pt (but not on Cu) from a solution of $SiCl_4$ or SiF_4 and KI in propylene glycol (8). Recently, Austin reported the electrodeposition of a-Si from SiX_4 (X: halogen) in various organic solvents (9).

In this study, cathodic deposition of a-Si from tetraethylorthosilicate ($Si(OC_2H_5)_4$) in acetic acid is presented.

Experimental

Commercial grade organic solvents and tetraethylorthosilicate (TEOS) were used without further purification.

The electrodeposition was carried out in an H-shaped vessel. The anode and cathode compartments were separated by a diaphragm of porous polytetrafluoroethylene. The solution of tetraethylorthosilicate in the organic solvents investigated in this study has a high resistance; reduction of the resistivity is achieved by adding tetramethylammonium chloride (TMAC) or tetraethylammonium chloride (TEAC), a usual additive for such purpose. TMAC and TEAC were dried under vacuum at 100°C. A cylindrical graphite rod was used as the anode and a nickel plate (99.99% pure) as the cathode. The effective area of the cathode was 2.3 cm^2. D-C current of 0.2 $mA/cm^2 \sim 20$ mA/cm^2 was supplied by a constant current power supply. In some cases, power was provided by a potentiostat, cathodic potential being measured relative to a silver-silver chloride electrode, which consisted of a mixture of silver powder and silver chloride powder in acetic acid with TMAC: Ag, $AgCl/CH_3COOH$, TMAC (0.12 mole/liter).

The electrode potential was 0.22V *vs.* SCE at 22°C. All experiments were carried out in flowing dry nitrogen. The deposits were investigated by reflection *IR* analysis, reflection high-energy electron diffraction (RHEED), and dispersive x-ray analysis in the scanning electron microscope.

Results and Discussion

Cathodic deposits were obtained on a nickel cathode from solutions of TEOS in acetic acid, propylene carbonate, and 1-chloropropane.

Table I shows typical experimental results of the electrodeposition from TEOS in acetic acid with TMAC at room temperature at a current density of 1 mA/cm^2. From this solution, bright blue deposits were obtained, which were tightly adhering to the nickel cathode. Acetone is effective to make the deposit homogeneous and also to decrease the resistivity of the solution. As shown in Table I, about a 20% increase in conductivity was observed by adding 2 cm^3 acetone to the solution of 60 cm^3 acetic acid, 4 cm^3 TEOS, and 2g TMAC. No deposit, however, was obtained from a solution with concentrations of acetone above 20 volume percent (v/o). A white precipitate became noticeable in the solution after passing a current for about 15 min. The formation of the precipitate was retarded by using distilled acetic acid. The white precipitate may be a product of hydrolysis of TEOS; *IR* spectra showed it to be a silica gel-like material. Table I indicates that the electrolysis from the solutions with higher concentration of TEOS gives lower weight gain (low current efficiency) (see 1st, 2nd, and 3rd lines). These solutions had the largest amounts of white precipitate, which adhered to the nickel cathode, preventing silicon deposition. The concentration of the supporting electrolyte affects the weight gain of the nickel cathode: There is an optimum concentration of TMAC to obtain the highest current efficiency (see 4th, 5th, and 6th lines). The highest current efficiency of about 60% calculated on the basis of a four-electron change was obtained from the solution consisting of 60 cm^3 acetic acid, 4 cm^3 TEOS, 2 cm^3 acetone, and 2g TMAC. The current efficiency decreases with increasing temperature; above 50°C no precipitate is formed in the solution and no deposit on the cathode is obtained; the evolution of hydrogen was observed.

Relations between the weight gain of the nickel cathode and coulombs passed at various current densities are shown in Fig. 1 for solutions containing 60 cm^3 acetic acid, 4 cm^3 TEOS, 2 cm^3 acetone, and 2g TMAC. As shown in this figure, the cathode increases its weight initially, but no change in weight is observed with further electrolysis. The weight gain and saturation by electrolysis were also observed on an n-type single crystal silicon cathode with relatively low resistivity. The saturation of the weight gain of nickel cathodes may be due to the low current efficiency on the pure silicon layer built on the nickel cathode. As can be seen from Fig. 1, the current efficiency decreases with increasing current density. Maximum weight gain of around 0.5 mg, which corresponds to 0.5 μm in thickness, is obtained at lower current density. No appreciable deposition was observed at current densities of 0.35 mA/cm^2 or less. Current *vs.* potential curves shown in Fig. 2 suggest that in this experimental condition hydrogen evolution begins to occur at 0.4 mA/cm^2. The potentials plotted were measured at the end of a 30 sec period of supplying the constant cathodic current. The electrode potential at 0.4 mA/cm^2 measured against the Ag/AgCl, acetic acid, TMAC reference electrode, was $-0.85V$ *vs.* NHE. Therefore, hydrogen evolution on the cathode may play an important role for the cathodic deposition on nickel. Low current efficiencies at higher current densities may be due to the co-evolution of hydrogen.

Nondispersive x-ray analysis in the scanning electron microscope showed that the deposits contain larger concentration of silicon. The intensity ratio of

Table I. Electrodeposition from solutions of $Si(OEt)_4$ in acetic acid

Acetic acid (cm^3)	$Si(OEt)_4$ (cm^3)	$(CH_3)_4NCl$ (g)	Acetone (cm^3)	Conductivity of the solution (S cm^{-1})	Current density (mA/cm^2)	Coulombs passed	Weight gain (mg)	Current efficiency (%)
60	1	2	2	1.2×10^{-3}	1	11	0.5	6 × 10
60	4	2	2	1.0×10^{-3}	1	11	0.5	6 × 10
60	10	2	2	0.7×10^{-3}	1	11	0.2	3 × 10
60	4	0.5	2	0.9×10^{-3}	1	15	0.1	1 × 10
60	4	2	2	1.0×10^{-3}	1	15	0.5	5 × 10
60	4	4	2	2.3×10^{-3}	1	15	0.2	2 × 10
60	4	2	0	0.8×10^{-3}	1	11	0.4	5 × 10

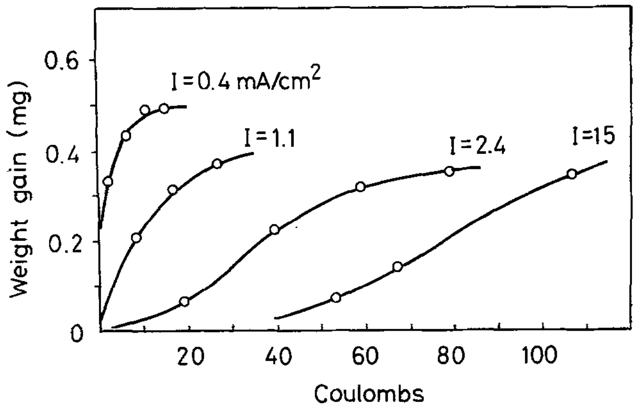

Fig. 1. The relation between the weight gain of the nickel cathode and coulombs passed for a solution containing 60 cm^3 acetic acid, 4 cm^3 Si(OEt)$_4$, 2 cm^3 acetone, and 2g (CH$_3$)$_4$NCl at room temperature.

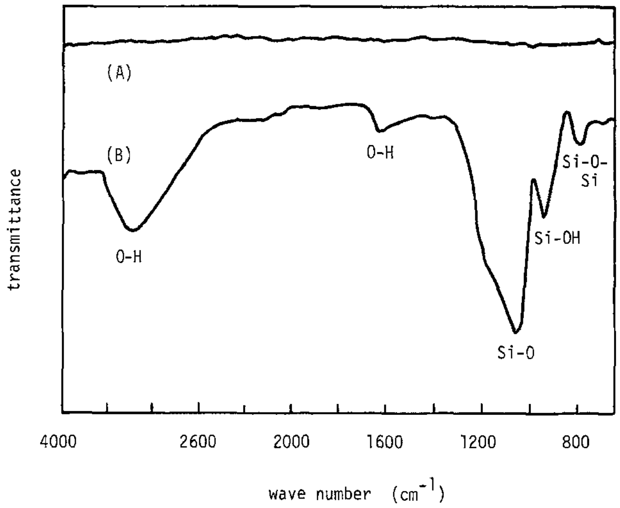

Fig. 3. *IR* reflection spectra. (A) Blue deposit obtained from the solution containing 4 cm^3 Si(OEt)$_4$, 60 cm^3 acetic acid, 2g TMAC, and 2 cm^3 acetone at a current density of 1 mA/cm^2. The thickness of the film is about 0.5 μm. (B) White deposit obtained from the solution containing 30 cm^3 acetic acid, 2 cm^3 Si(OEt)$_4$, 10 cm^3 acetone, and 0.05 cm^3 pyridine at a current density of 4 mA/cm^2. The thickness of the film is about 0.7 μm.

SiKα and NiKα, I_{Si}/I_{Ni}, of the nickel coated with silicon of about 0.5 μm thickness was 3.5. As shown in Fig. 3(A), *IR* reflection spectra of the deposits exhibit no absorption in the wave number range of 4000-600 cm^{-1}. X-ray diffraction patterns showed only those due to the nickel substrate. A RHEED investigation using Hitachi HU-12 A showed no reflection ring or spot from crystallization. It can be concluded from these results that the deposits consist of amorphous silicon.

As shown in Table I, the weight gain (current efficiency) on the cathode depends strongly on the concentration of TMAC in the solution. Attempts were made to plate silicon from a solution with a different supporting electrolyte, tetrabutylammonium chloride and tetrabutylammonium perchlorate. The results were similar to those obtained with TMAC. The conductivity of the solution of TEOS in acetic acid is markedly increased by the addition of pyridine. Pyridine reacts with acetic acid to produce a quaternary amine, which is effective as the supporting electrolyte. From the solution of TEOS, acetic acid, pyridine, and acetone, a whitish-gray deposit was obtained on the nickel cathode. A typical relation between the weight gain of the nickel cathode and coulombs passed at room temperature is shown in Fig. 4. The composition of the solution was 30 cm^3 acetic acid, 10 cm^3 acetone, 0.05 cm^3 pyridine, and 2 cm^3 TEOS, and the current density was about 4 mA/cm^2. In this case, the weight gain of the cathode increases approximately linearly with the number of coulombs passed. The current efficiency decreased with increasing current density; efficiencies of about 20 and 5% were obtained at 0.8 and 10 mA/cm^2, respectively.

Nondispersive x-ray analysis showed the deposits to contain silicon. The ratio, I_{Si}/I_{Ni}, of the sample 0.5 μm in thickness was 0.8. *IR* reflection spectra of the deposits were similar to those of silica gel and of the white precipitate in the solution as shown in Fig. 3(B). A deposit of silica gel should lose its weight upon annealing in inert gas at 400°C. However, no weight change was observed after heating the sample at 400°C for 2 hr in flowing argon. These results suggest that the deposits from the solution with pyridine contain only a small amount of silica gel-like materials.

A white deposit was obtained on the nickel cathode from the solutions of TEOS in 1-chloropropane with TMAC as the supporting electrolyte. In a dry atmo-

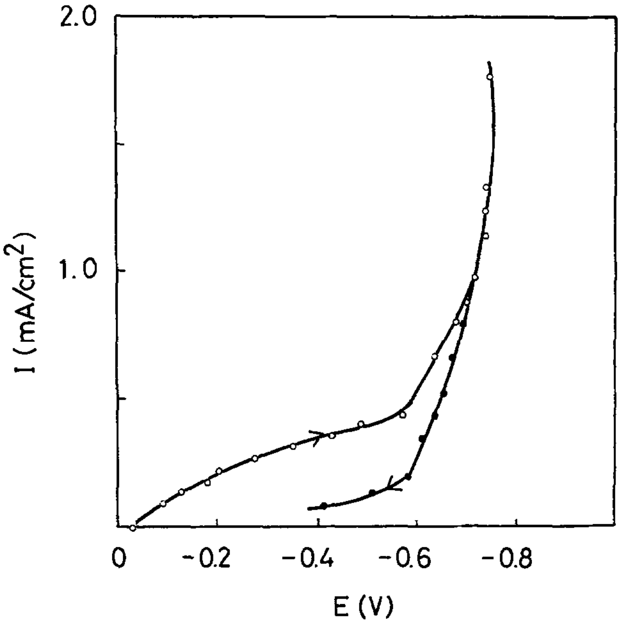

Fig. 2. Current density, *I*, vs. potential, *E*, (vs. Ag/AgCl, CH$_3$COOH, TMAC (0.12 mole/liter) curve for the solution containing 60 cm^3 acetic acid, 4 cm^3 Si(OEt)$_4$, 2 cm^3 acetone, and 2g (CH$_3$)$_4$NCl at room temperature.

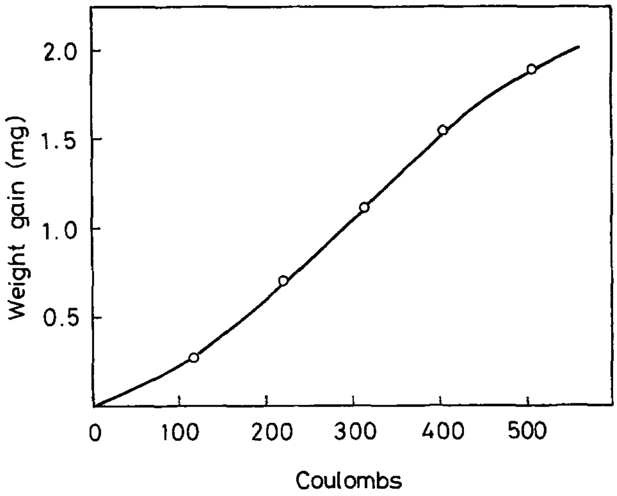

Fig. 4. The relation between the weight gain of the nickel cathode and coulombs passed for a solution containing 30 cm^3 acetic acid, 2 cm^3 Si(OEt)$_4$, 10 cm^3 acetone, and 0.05 cm^3 pyridine at room temperature.

sphere, no deposit was observed; in a wet atmosphere, a white precipitate was formed in the solution and a white deposit was obtained, with a maximum weight gain of about 0.5 mg. Nondispersive x-ray analysis showed that the deposit contained silicon, and I_{Si}/I_{Ni} of the sample 0.5 μm in thickness was 0.56. The *IR* reflection spectra exhibited peaks of Si-O modes; evidently, the white deposits contained silicon-oxygen compounds. Similar white deposits were obtained from a solution of TEOS in propylene carbonate.

In all cases of electrodeposition from solutions containing TEOS as a silicon source, the deposits were observed after the white precipitate of a silica gel-like material appeared in the solution. Yet the deposit on the cathode is only partly SiO_2. It is possible that hydrogen evolved on the cathode breaks Si—O bonds in the silica gel-like material and some ions containing silicon are reduced electrochemically on the nickel cathode. No deposit was obtained on copper, gold, and platinum used as cathodes. Clarification of the electrodeposition mechanism requires further study.

Summary

White, whitish-gray and blue deposits were obtained on the nickel cathode by the electrolysis of the solution of TEOS in organic solvents. Nondispersive x-ray analysis showed the deposits to contain silicon. However, it is doubtful whether the white and whitish-gray deposits are amorphous silicon or a silicon-oxygen compound, because *IR* spectra of these deposits were similar to those of silica gel, and the intensity ratios of SiKα to NiKα of these deposits were considerably lower than the ratio for the blue deposit. On the other hand, the blue deposits, which were obtained from the solution of TEOS in acetic acid, did not show the absorption due to Si—O and O—H modes, and had a high intensity ratio of SiKα to NiKα. The electrodeposition of thin films of amorphous silicon from the solution of TEOS in acetic acid seems promising, but problems such as the control of hydrogen content and the doping with donors or acceptors remain to be investigated before it can be put in practical use.

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Photoactivation of CdSe Films for Photoelectrochemical Cells

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ABSTRACT

The efficiency of photoelectrochemical cells with thin-film CdSe electrodes can be enhanced by illuminating the semiconductor electrode in salt solution under closed-circuit condition. The photoactivation mechanism involves the photooxidation of CdSe to elemental selenium with concomitant release of cadmium ions into the salt solution and subsequent reductive dissolution of the resulting layer of elemental selenium. This method can be controlled more precisely than acid etching and hence is more suitable for large scale application.

The conversion of solar to electrical energy with moderate efficiency has been demonstrated by means of photoelectrochemical (PEC) cells with CdSe photoanodes (1-4). The performance of these semiconductor electrodes can often be greatly improved by limited acid etching. Heller *et al.* (2) showed an inverse correlation between the presence of surface states within the forbidden gap of the semiconductor and the efficiency of PEC cells. They suggested that acid etching of single crystals of CdSe removes the surface states which act as barrier traps and recombination centers.

A more easily controlled activation method particularly suitable for thin-film II-VI semiconductor electrodes is a photoactivation process developed in our work on PEC cells (5). In this process, the thin-film CdSe electrode was immersed together with a platinum counterelectrode in a salt solution (*e.g.*, NaCl) and illuminated under closed-circuit condition. When the photoactivated CdSe thin-film electrode was subsequently used as the photoanode in a photoelectrochemical cell with polysulfide solution, both the photocurrent and the fill factor were enhanced. Recently Hodes (6) reported a "photoetching" effect of 0.1M H_2SO_4 on $CdSe_{0.65}Te_{0.35}$ electrodes which could be of

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Key words: semiconductor, photovoltaic, cell.