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(54) **ALUMINUM ELECTROPLATING SOLUTION**

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(57) **ABSTRACT**

The purpose of the present invention is to provide an aluminum electroplating solution that allows aluminum electroplating to be conducted efficiently and in a short period of time, can increase the amount of electricity in the current of electroplating, and has high solubility in a nonaqueous solvent. This aluminum electroplating solution is characterized by comprising an aluminum metal salt, an ionic liquid obtained by an organic compound forming an ion pair with the aluminum metal salt, and an organic solvent having a dielectric constant of 8 or less. It is preferable for the volume percentage of the organic solvent in relation to the total volume of the ionic liquid and the organic solvent to be at least 30%, and for at least one of the following to be included as the organic solvent having a dielectric constant of 8 or less: hexane, toluene, diethyl ether, ethylacetate, cyclohexane, xylene, benzene, naphthalene, heptane, cyclopentyl methyl ether, and dioxane.

## ALUMINUM ELECTROPLATING SOLUTION

### TECHNICAL FIELD

**[0001]** The present invention relates to an aluminum electroplating solution using an organic solvent (non-aqueous solvent).

### BACKGROUND ART

**[0002]** It is difficult to conduct an aluminum electroplating in aqueous solution type plating bath, because aluminum has a high affinity to oxygen and has a negative equilibrium potential compared to hydrogen. Thus, in the aluminum electroplating, many organic solvent plating solutions have been studied. Typical ones of this organic solvent type plating bath include  $\text{AlCl}_3$  and  $\text{LiAlH}_4$  or  $\text{LiH}$  dissolved in ether, or  $\text{AlCl}_3$  and  $\text{LiAlH}_4$  dissolved in THF (tetrahydrofuran). However, all of these plating baths contain  $\text{LiAlH}_4$  or  $\text{LiH}$  which are very active in the baths, and thus react with oxygen or moisture, when being present, to be decomposed and lower a current efficiency and shorten a bath life also. Under the circumstances, Patent Literatures 1 and 2 etc. report a molten salt electrolytic plating solution containing a dimethylsulfone solvent as a safe and low-cost plating solution.

**[0003]** Recently, Patent Literatures 3 and 4 etc. suggest an aluminum electroplating method using, as a plating bath, a molten salt comprising 1-alkyl or 1,3-dialkylimidazolium halide, quarternary ammonium salt or alkylpyridinium halide, and aluminumhalide etc. However, plating states of these plating baths are largely changed due to a mixing of moisture, and thus even if an electroplating is conducted under constant plating conditions, a uniform plating coating is not always obtained.

### CITATION LIST

#### Patent Literature

- [0004]** [Patent Literature 1] JP 2004-76031 A
- [0005]** [Patent Literature 2] JP 2006-161154 A
- [0006]** [Patent Literature 3] JP 62-70592 A
- [0007]** [Patent Literature 4] JP 1-272788 A

### SUMMARY OF INVENTION

#### Technical Problem

**[0008]** However, conventional nonaqueous electrolytes generally have a low solubility to an aluminum salt, it is difficult to conduct a plating treatment at a heavy current in a short period of time, and a plating operation cannot be efficiently conducted. Additionally, when oxygen or moisture are present in an electrolyte, there were problems that an aluminum salt reacts with those to be decomposed to lower a current efficiency, result in a deteriorated plating finish, and deteriorate the electrolyte.

**[0009]** In addition to these problems, in case of a high temperature molten salt type nonaqueous electrolyte,  $100^\circ\text{C}$ . or more is necessary in an operation and there was a problem that it was impossible to conduct an operation at an ordinary temperature. Additionally, in case of an ordinary temperature molten salt type nonaqueous electrolyte, an operable range is very narrow, and when a concentration of an aluminum metal salt is increased for decreasing a defect such as a non-precipitation of a plating film, a viscosity of a liquid becomes high,

and thus there were problems that a precipitation speed of plating was decreased together with a deteriorated plating level.

**[0010]** Thus, the purpose of the present invention is to solve the above problems and to provide an aluminum electroplating solution that allows aluminum electroplating to be conducted efficiently and in a short period of time, can increase the amount of electricity in the current of electroplating, and has a high solubility in a nonaqueous solvent.

#### Solution to Problem

**[0011]** The aluminum electroplating solution of the present invention is characterized by comprising an aluminum metal salt, an ionic liquid obtained by an organic compound forming an ion pair with the aluminum metal salt, and an organic solvent having a dielectric constant of 8 or less. It is preferable for the volume fraction of the organic solvent in relation to the total volume of the ionic liquid and the organic solvent to be at least 30%, and for at least one of the following to be included as the organic solvent having a dielectric constant of 8 or less: hexane, toluene, diethyl ether, ethylacetate, cyclohexane, xylene, benzene, naphthalene, heptane, cyclopentyl methyl ether, and dioxane.

**[0012]** Other objects, features and advantages of the invention will become apparent from the following description of the embodiments of the invention.

#### Advantageous Effects of Invention

**[0013]** According to the present invention, a precipitation efficiency of plating is enhanced, a uniformity of a film thickness can be improved. Additionally, by applying the above plating, it comes to be possible to provide parts having a steric shape with a uniform plating applied.

### DESCRIPTION OF EMBODIMENTS

**[0014]** Working embodiments of the present invention are explained below.

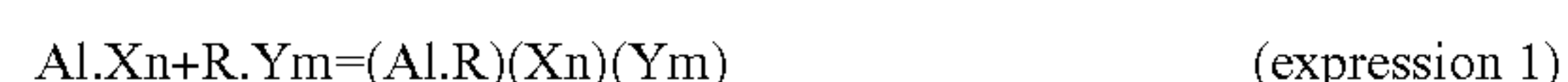
**[0015]** The aluminum metal salt used as an aluminum source can include an aluminumhalide. The aluminumhalide used can include an anhydrous salt such as aluminum chloride and aluminum bromide. When an aluminum concentration in a plating solution in relation to the organic compound forming an ion pair with the aluminum metal salt is equimolar or less, a precipitation speed of plating is remarkably lowered and thus a higher concentration results in a better precipitation uniformity of plating. It is better that the aluminum concentration in the plating solution in relation to the organic compound forming an ion pair with the aluminum metal salt is equimolar or more, preferably 1.5 times or more, more preferably 3 times or more.

**[0016]** The organic compound forming an ion pair with the aluminum metal salt used can include a halide of an organic compound cation such as dialkyl imidazolium salt, aliphatic phosphonium salt, and quaternary ammonium salt. The dialkyl imidazolium salt suitably used can include 1,3-dialkylimidazoliumhalide which includes 1-ethyl-3-methylimidazolium chloride ([EMIM].Cl), 1-ethyl-3-methylimidazolium bromide ([EMIM].Br), 1-ethyl-3-methylimidazolium iodide ([EMIM].I), 1-butyl-3-methylimidazolium chloride ([BMIM].Cl), 1-butyl-3-methylimidazolium bromide ([BMIM].Br), 1-butyl-3-methylimidazolium iodide ([BMIM].I) etc. Additionally, the aliphatic phosphonium salt suitably used can include ethyltributyl phosphonium chloride



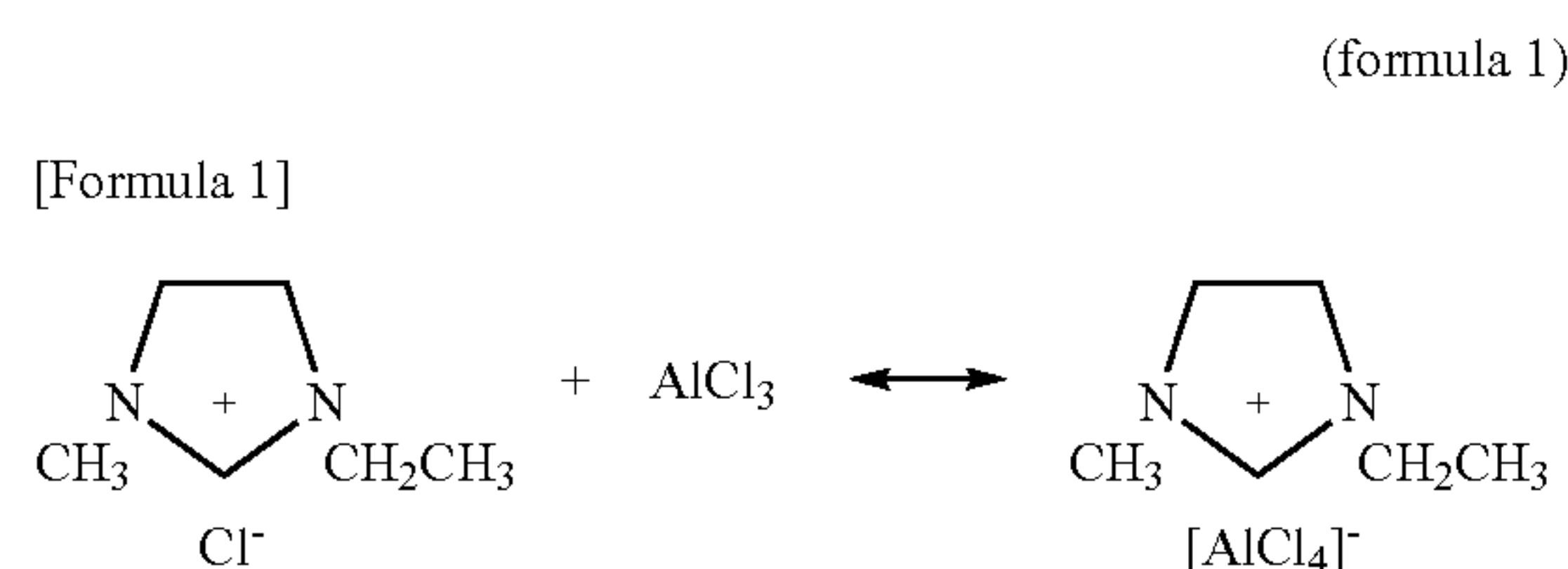
([EBP].Cl), ethyltributyl phosphonium bromide ([EBP].Br), ethyltributyl phosphonium iodide ([EBP].I) etc. The quaternary ammonium salt suitably used can include tetraethyl ammonium bromide ([E4N].Br), trimethylethyl ammonium chloride ([M3EN].Cl), tetrabutyl ammonium chloride ([Bu4N].Cl) etc.

**[0017]** An ionic liquid having an ion pair formed is formed by mixing the above-mentioned aluminum metal salt with the organic compound forming an ion pair with the aluminum metal salt according to the following reaction.



**[0018]** (In the expression 1, X and Y represent a halide, R represents an organic compound cation, and n and m represent a valence number and are an integer of from 1 to 4.)

**[0019]** The following example is a reaction in case of using aluminum chloride as the aluminum metal salt and using 1-ethyl-3-methylimidazolium chloride as the organic compound forming an ion pair with the aluminum metal salt.



**[0020]** As mentioned above, a mixing of an aluminum salt with an organic compound such as a dialkylimidazolium salt forms an ion pair to obtain a melt (ionic liquid). This ionic liquid can function as an electroplating solution. However, although it is desired that a concentration of aluminum is high as a plating solution, when a molar ratio of the aluminum metal salt in relation to the organic compound forming an ion pair with the aluminum metal salt is e.g. 3 or more, a viscosity becomes higher to lower a fluidity due to a higher concentration of aluminum, and a uniform plating precipitation cannot come to be obtained from such an ionic liquid. Thus, in the present invention, by dissolving an ionic liquid having a high viscosity into an organic solvent, even the molar ratio of 3 or more can lower a viscosity to be able to be suitably used as a plating solution. Additionally, although a higher volume fraction of the organic solvent results in a relatively lower ion concentration of aluminum, an apparent diffusion coefficient becomes large due to a lowering of a viscosity, and thus a large electric current can come to be uniformly applied to a surface to be plated. Thus, a uniform plating can be obtained on a substrate face.

**[0021]** It is preferred that a nonpolar solvent having a dielectric constant of 8 or less is used as the organic solvent. In case of using a polar organic solvent having a high dielectric constant, the aluminum and the organic compound having an ion pair formed are dissociated and a precipitation efficiency of a plating becomes lowered. Reasons therefor are because the Coulomb force between positive and negative ions in the ionic liquid is in inverse proportion to a dielectric constant of a medium, a higher dielectric constant of a solvent becomes a lower Coulomb force, a dissociation of a metal salt becomes easy, and a dissociation of an ion pair of the aluminum metal salt and the organic compound becomes easy. Thus, a dielectric constant of the organic solvent is preferably 8 or less, more preferably 5 or less. Such an organic solvent

can include hexane (dielectric constant of 2.0), toluene (dielectric constant of 2.4), diethyl ether (dielectric constant of 4.3), ethylacetate (dielectric constant of 6.0), cyclohexane (dielectric constant of 2.0), xylene (dielectric constant of 2.5), benzene (dielectric constant of 2.3), naphthalene (dielectric constant of 2.5), heptane (dielectric constant of 1.9), cyclopentyl methyl ether (dielectric constant of 4.8), and dioxane (dielectric constant of 2.1), and any one or plural kinds thereof can be used. Additionally, a boiling point of the organic solvent is preferably 40° C. or more, and a too low boiling point is not preferred because countermeasures against an exhalation and flammability etc. of the organic solvent such as a sealing and cooling etc. become excessive. Additionally, a volume fraction of the organic solvent in relation to a total volume of the ionic liquid and the organic solvent is preferably 30 vol % or more, further preferably 50 vol % or more, desirably 75 vol % or more. However, a too high volume fraction of the organic solvent results in a too low ion concentration of aluminum, and more than 90 vol % causes a lowering of a current efficiency of plating. Thus, the volume fraction of the organic solvent is preferably 90 vol %.

**[0022]** When a transition metal salt of Ni, Co, or Cu etc. or a refractory metal salt of Ti, W or Mo is added as a base metal salt in addition to an aluminum salt, these elements are contained in the resulting plating film and a thermal stability can be enhanced. In case of e.g. nickel, nickel chloride or nickel sulfate etc. can be added so as to be a concentration of from 0.01 to 20 mol % while an amount of the aluminum salt added can be controlled so that a total metal salt concentration of the nickel salt and the aluminum salt is constant. Similarly, also in case of other base metal salts, a metal salt etc. with a chloride can be added.

**[0023]** From the viewpoint of an operability, a plating treatment temperature is preferably from 10 to 60° C., further desirably 40° C. or less. When the temperature is less than 10° C., a viscosity becomes high and a whole plating film has a tendency to become black.

**[0024]** When an aluminum electroplating is conducted at an electric current density of from 0.01 to 10 A/dm<sup>2</sup> by a DC or a pulse electric current as plating conditions, a current efficiency becomes good and a uniform plating can be made. It is not preferred that an electric current density is too high, because an organic compound is decomposed, a plating layer is non-uniformized and further a current efficiency becomes lowered. It is desired that a plating is conducted in a dry inert gas atmosphere because the plating solution is unstable to oxygen or moisture.

**[0025]** In case of conducting a continuous plating, it is necessary to keep an Al ion concentration in a bath at a constant range by supplying an Al ion in a plating bath. In this instance, when an anode electrode is an aluminum-made anodic dissolution, an Al ion is automatically supplied according to an amount of electricity in the current, an Al ion concentration can be kept at a constant range without supplying an aluminum halide, and further a bath composition is not changed.

**[0026]** The organic solvent used for washing, after the plating, includes saturated aliphatic hydrocarbons such as hexane and dodecane, and aromatic hydrocarbons such as benzene, toluene, hexylbenzene and dodecylbenzene. They do not adversely affect even if being mixed into a plating solution. Of them, aromatic hydrocarbons having an alkyl substituent, particularly alkylbenzene having an alkyl substituent of 8 or less carbon atom, is especially preferred because they do not



adversely affect a plating even if being mixed into a plating solution. A boiling point of the organic solvent is preferably 40° C. or more, and a too low boiling point is not preferred because countermeasures against an exhalation and flammability etc. of the organic solvent such as a sealing and cooling etc. become excessive.

**[0027]** The present invention is explained in more detail by referring to the following examples, but the present invention is not limited to these descriptions.

#### Example 1

**[0028]** 1-ethyl-3-methylimidazolium chloride (commercially available from KANTO CHEMICAL CO., INC.; [EMIM]Cl) and anhydrous aluminum chloride (Wako Pure Chemical Industries, Ltd., AlCl<sub>3</sub>) were used. A weighing capacity was conducted in a glove box at a humidity set to 5% and a temperature set to 25° C., and AlCl<sub>3</sub> was added so as to be a molar ratio of [EMIM]Cl:AlCl<sub>3</sub>=1:3 to obtain a 100 ml melt. The above mentioned melt was dissolved in 300 ml toluene (Wako Pure Chemical Industries, Ltd.), and a plating solution was prepared so as to be 400 ml in a total volume. The resulting electrolyte 400 ml was charged into a polypropylene-made electrolytic bath having longitudinal×transversal×height of 100 mm×50 mm×100 mm.

**[0029]** Next, an aluminum plate of purity 99.9% having longitudinal×transversal of 75 mm×75 mm and a thickness of 2 mm, as an anode electrode, and a copper foil having longitudinal×transversal of 50 mm×50 mm and a thickness of 0.1 mm, as a cathode electrode, were facing-positioned at an interval of 30 mm each other in the electrolytic bath, and were immersed in the electrolyte. A lead wire for connection with the electrodes are passed through at a state that a lid of the electrolytic bath is airtight, and were connected with a power supply.

**[0030]** After the above operations were conducted in a glove box, it was taken out outside.

**[0031]** An aluminum electroplating was conducted at an electric current density -10 mA/cm<sup>2</sup> for 20 minutes or an electric current density -20 mA/cm<sup>2</sup> for 10 minutes by using a constant electric current source, to form an aluminum plating film on a surface of a copper foil. It was conducted at a voltage of 3V or less in the plating. Then, an evaluation of a current efficiency and an observation of a surface state of the plating film were conducted. The current efficiency was determined by determining a precipitation amount of aluminum by actual measurement, comparing this to a precipitation amount precalculated based on an electric current value of a coulomb meter, and determining a ratio to the latter precipitation amount calculated as a percentage.

**[0032]** In result of conducting as above, a plating state was good. Additionally, in result of measuring film thicknesses of five portions in a copper foil face, good results of a plating film thickness of 4 μm and a distribution within 5% were obtained. Additionally, the current efficiency was as good as 97%.

**[0033]** As clear from these results, it was found that, when the solvent and the solute as in the present Example were used, a large electric current of a electroplating can be conducted, a plating of aluminum can be achieved efficiently and in a short period of time, and further a current efficiency was good, troubles due to a deterioration of an electrolyte were avoided, good plating states having a good uniformity were able to be obtained.

#### Examples 2 to 12

**[0034]** Aluminum chloride salts AlCl<sub>3</sub> were dissolved by using organic compounds and organic solvents shown at Table 1 so as to become one of several salt concentrations A (mol/l), to prepare plating solutions of Examples 2 to 12 as well as in Example 1.

**[0035]** An aluminum electroplating was conducted at an electric current density -10 mA/cm<sup>2</sup> for 20 minutes or an electric current density -20 mA/cm<sup>2</sup> for 10 minutes by using a constant electric current source. Then, an evaluation of a current efficiency and an observation of a surface state of the plating film were conducted. It was conducted at a voltage of 3V or less in the plating. The current efficiency was determined by determining a precipitation amount of aluminum by actual measurement, comparing this to a precipitation amount precalculated based on an electric current value of a coulomb meter, and determining a ratio to the latter precipitation amount calculated as a percentage. The results are shown at Table 1.

**[0036]** As clear from these results, when the solvent and the solute as in Examples 1 to 12 were used, a large electric current of a electroplating can be conducted, a plating of aluminum can be achieved efficiently and in a short period of time, and further a current efficiency was good, troubles due to a deterioration of an electrolyte were avoided, good plating states can be obtained. A higher concentration of the aluminum salt was able to enhance a current efficiency in the plating. Additionally, a higher concentration of the organic solvent was able to lower a viscosity and was able to decrease a film thickness variation. Furthermore, when a base metal other than an aluminum salt is added as in Examples 4 and 5, a current efficiency may be lowered but a film thickness variation of the plating film was able to be decreased.

TABLE 1

	Metal salt	Organic compound	Organic solvent	Second metal salt	Bath temperature ° C.
Example 2	AlCl <sub>3</sub>	[EMIM]•Cl	toluene		30
	80 mol %	20 mol %	30 vol %		
Example 3	AlCl <sub>3</sub>	[EMIM]•Cl	toluene		30
	80 mol %	20 mol %	50 vol %		
Example 4	AlCl <sub>3</sub>	[EMIM]•Cl	toluene	NiCl <sub>2</sub>	30
	70 mol %	22 mol %	50 vol %	8 mol %	
Example 5	AlCl <sub>3</sub>	[EMIM]•Cl	toluene	TiCl <sub>4</sub>	30
	70 mol %	25 mol %	30 vol %	5 mol %	
Example 6	AlCl <sub>3</sub>	[EMIM]•Cl	xylene		30
	80 mol %	20 mol %	80 vol %		



TABLE 1-continued

Example 7	AlCl <sub>3</sub>	[EMIM]•Cl	cyclohexane	30
	80 mol %	20 mol %	75 vol %	
Example 8	AlCl <sub>3</sub>	[EMIM]•Cl	diethyl ether	30
	80 mol %	20 mol %	75 vol %	
Example 9	AlCl <sub>3</sub>	[BMIM]•Cl	toluene	30
	67 mol %	33 mol %	80 vol %	
Example 10	AlBr <sub>3</sub>	[EMIM]•Br	toluene	30
	80 mol %	20 mol %	80 vol %	
Example 11	AlCl <sub>3</sub>	[EBP]•Cl	toluene	30
	80 mol %	20 mol %	80 vol %	
Example 12	AlCl <sub>3</sub>	[M3EN]•Cl	toluene	30
	80 mol %	20 mol %	80 vol %	
Comparative Example 1	AlCl <sub>3</sub>	[EMIM]•Cl		30
	80 mol %	20 mol %		
Comparative Example 2	AlCl <sub>3</sub>	[EMIM]•Cl	propylene carbonate	30
	80 mol %	20 mol %	80 vol %	
Comparative Example 3	AlCl <sub>3</sub>	[EMIM]•Cl	acetonitrile	30
	80 mol %	20 mol %	80 vol %	

	Electric current mA/cm <sup>2</sup>	Period of time (minute)	Current efficiency %	Plating film thickness μm	Crystallinity	Film thickness variation %
Example 2	20	10	88	3.5	dense	10
Example 3	20	10	95	3.9	dense	7
Example 4	10	20	90	3.7	dense	9
Example 5	10	20	88	3.6	dense	6
Example 6	20	10	96	4	dense	7
Example 7	20	10	94	3.8	dense	6
Example 8	20	10	93	3.7	dense	8
Example 9	20	10	95	3.9	dense	8
Example 10	20	10	96	4	dense	6
Example 11	20	10	90	3.7	dense	8
Example 12	20	10	90	3.7	dense	8
Comparative Example 1	20	10	15	0.5	nondense	40
Comparative Example 2	20	10	2	0.1	nondense	50
Comparative Example 3	20	10	2	0.1	nondense	60

## Example 13

[0037] According to the plating method as well as in Example 1, a plating was conducted onto a material to be plated which is a copper foil having a center folded at 90 degree in the L-shape. In result of measuring film thicknesses of five portions of a copper foil face, good results of a plating film thickness of 4 μm and a distribution within 8% were obtained. The current efficiency was as good as 97%.

[0038] As clear from these results, it was found that, when the solvent and the solute as in the present Example were used, a large electric current of a electroplating can be conducted, a plating of aluminum can be achieved efficiently and in a short period of time, and parts having a uniform plating applied were able to be provided even from a steric shape.

## Comparative Example 1

[0039] A plating was conducted by using, as a plating solution, an ionic liquid comprising 1-ethyl-3-methylimidazolium chloride (20 mol %) and aluminum trichloride (80 mol %) as well as in Example 1. In this case, although it was conducted at an electric current density of 20 mA/cm<sup>2</sup>, a good plating was not able to be obtained to form a plating film having a black burned surface of an aluminum plating. Additionally, a viscosity of the plating solution was high, and thus a distribution of a film thickness became large.

## Comparative Example 2

[0040] A plating was conducted by using, as a plating solution, an ionic liquid comprising 1-ethyl-3-methylimidazolium chloride (20 mol %) and aluminum trichloride (80 mol %), as well as in Example 1, dissolved in a polar solvent propylene carbonate (dielectric constant of 65). In this case, although it was conducted at an electric current density of 20 mA/cm<sup>2</sup>, a good plating was not able to be obtained and almost aluminum was not precipitated. It is understood that, when the ionic liquid is dissolved in such a polar solvent, the aluminum salt and the organic compound having an ion pair formed are dissociated to inhibit a plating reaction.

## Comparative Example 3

[0041] A plating was conducted by using, as a plating solution, an ionic liquid comprising 1-ethyl-3-methylimidazolium chloride (20 mol %) and aluminum trichloride (80 mol %), as well as in Example 1, dissolved in a polar solvent acetonitrile (dielectric constant of 38). In this case, although it was conducted at an electric current density of 20 mA/cm<sup>2</sup>, a good plating was not able to be obtained and almost aluminum was not precipitated.

[0042] It should be further understood by those skilled in the art that although the foregoing description has been made on embodiments of the invention, the invention is not limited thereto and various changes and modifications may be made

without departing from the spirit of the invention and the scope of the appended claims.

1. An aluminum electroplating solution comprising:  
an aluminum metal salt,  
an ionic liquid obtained by an organic compound forming an ion pair with the aluminum metal salt; and  
an organic solvent having a dielectric constant of 8 or less, wherein a volume fraction of the organic solvent in relation to a total volume of the ionic liquid and the organic solvent is 75% or more.
2. (canceled)
3. The aluminum electroplating solution according to claim 1, wherein the aluminum metal salt comprises at least aluminum halide.
4. The aluminum electroplating solution according to claim 1, wherein the organic solvent is at least one kind selected from the group consisting of hexane, toluene, diethyl ether, ethylacetate, cyclohexane, xylene, benzene, naphthalene, heptane, cyclopentyl methyl ether, and dioxane.
5. The aluminum electroplating solution according to claim 1, wherein the organic compound forming an ion pair with the aluminum metal salt comprises at least one kind

selected from the group consisting of dialkyl imidazolium salt, aliphatic phosphonium salt, and quaternary ammonium salt.

6. The aluminum electroplating solution according to claim 1, wherein a molar ratio of the aluminum metal salt in relation to the organic compound forming an ion pair with the aluminum metal salt is 1 or more.

7. The aluminum electroplating solution according to claim 1, wherein the aluminum electroplating solution is obtained by mixing the aluminum metal salt with the organic compound forming an ion pair with the aluminum metal salt to prepare the ionic liquid, and then mixing the ionic liquid with the organic solvent.

8. The aluminum electroplating solution according to claim 1, wherein the aluminum electroplating solution comprises a base metal salt other than an aluminum metal salt.

9. The aluminum electroplating solution according to claim 1, wherein a molar ratio of the aluminum metal salt in relation to the organic compound forming an ion pair with the aluminum metal salt is 3 or more.

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