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Long-Term Sustainable Aluminum Precursor Solution for Highly Conductive Thin Films on Rigid and Flexible Substrates

Hye Moon Lee,*[,†] Jung Yoon Seo,[§] Areum Jung,[†] Si-Young Choi,[‡] Seung Hwan Ko,[∥] Jeongdai Jo,[⊥] Seung Bin Park,[§] and Duckshin Park[#]

[†]Powder & Ceramics Division and [‡]Advanced Characterization and Analysis Group, Korea Institute of Materials Science (KIMS), Changwon 642-831, Korea

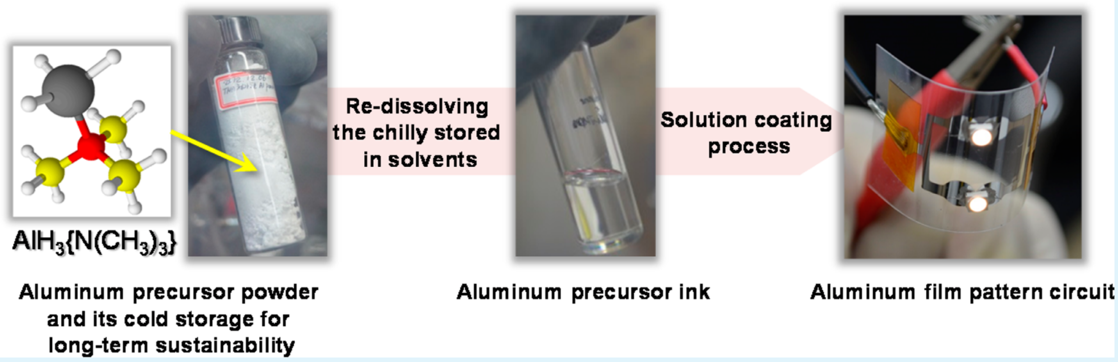
[§]Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea

[∥]Department of Mechanical & Aerospace Engineering, Seoul National University, Seoul 151-744, Korea

[⊥]Department of Printed Electronics, Korea Institute of Machinery and Materials (KIMM), Daejeon 305-343, Korea

[#]Eco-Transfer Research Division, Korea Raillroad Research Institute (KRRI), Uiwang 437-757, Korea

S *Supporting Information*



ABSTRACT: To fabricate the highly conductive Al film via a solution process, AlH_3 etherates have been a unique Al source despite their chemical instability in solvents and thus lack of long-term sustainability. Herein, we suggest an innovative solution process to overcome the aforementioned drawbacks in AlH_3 etherates; AlH_3 aminates powder, which can be stored in low temperature surroundings and redissolved in solvents whenever it is needed. Since refrigeration of AlH_3 aminates, $AlH_3\{N(CH_3)_3\}$, was very effective to prevent its chemical degradation, Al film with excellence and uniformity in electrical and mechanical properties was successfully fabricated even by the 180-day stored $AlH_3\{N(CH_3)_3\}$ dissolved in solvents. Moreover, the applicability of long-term stored $AlH_3\{N(CH_3)_3\}$ to electronic devices was experimentally demonstrated by the successful operation of LED lamps connected to the Al pattern films on glass, PET, and paper substrates.

KEYWORDS: *solution process, aluminum, precursor, conductive film, electrodes*

INTRODUCTION

Printed electronics are drawing tremendous amounts of attention as the key to the development of future electronics such as flexible and wearable electronics. Solution-processable electronic materials are the most important part when attempting to develop successful printed electronics processes. A solution process using colloidal ink (i.e., well-dispersed metallic nanoparticles in a specific solvent) is one of the most cost-effective methods for the preparation of highly conductive metallic features on both rigid and flexible substrates at low-temperature surroundings.[1−14] The colloidal ink used in the solution process generally consists of silver (Ag) or gold (Au) nanoparticles due to their high electrical conductivity as well as low reactivity with oxygen and moisture. However, Ag and Au are very expensive and continue to increase in price such that alternative metals with high electrical conductivity but low prices are required for the cost-effective preparation of electronic devices with highly conductive metallic features on substrates.

To this end, aluminum (Al) has been considered as the best candidate metal source with which to fabricate electrodes and electric circuits with high electrical performance levels due to its low cost and low work function value.[6,11−14] However, due to the drastic oxidation of Al nanoparticles, it has been extremely challenging to prepare the colloidal Al-ink without oxidation problems, especially when their size is smaller than 10 nm in

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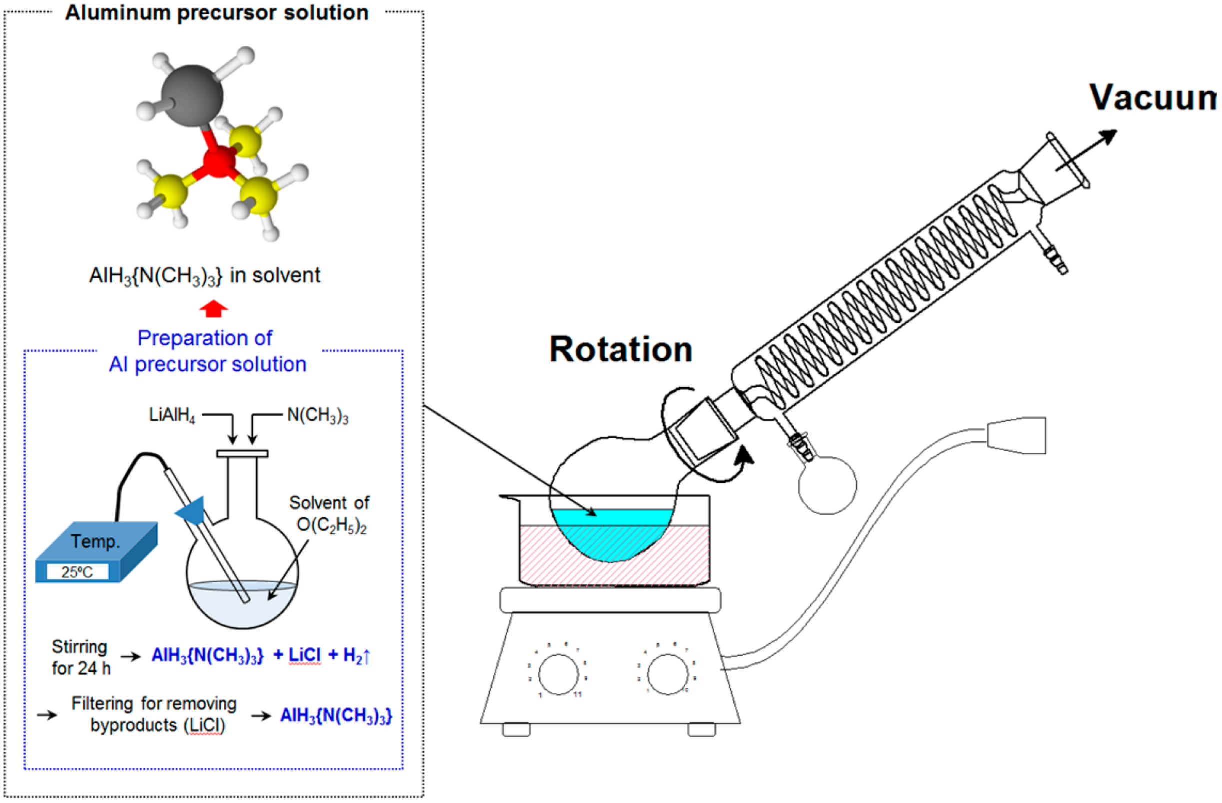
Scheme 1. Experimental Procedure for Preparation of Al Precursor $AlH_3\{N(CH_3)_3\}$ Powders



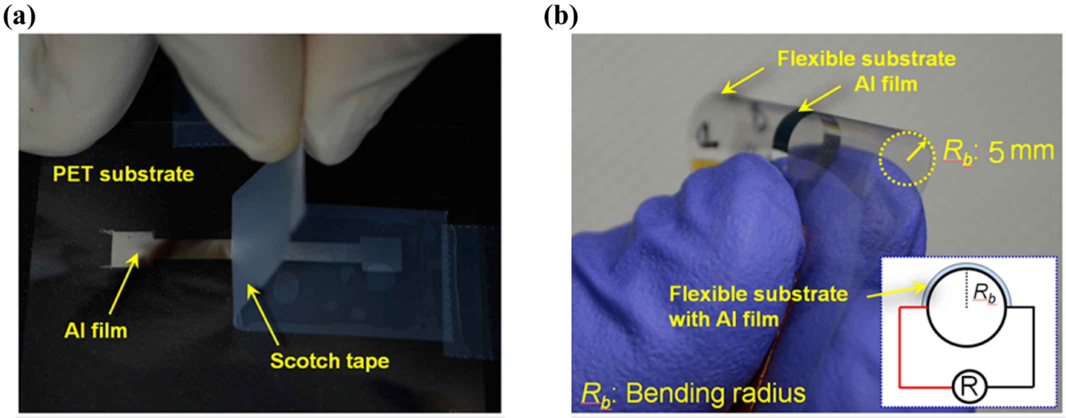
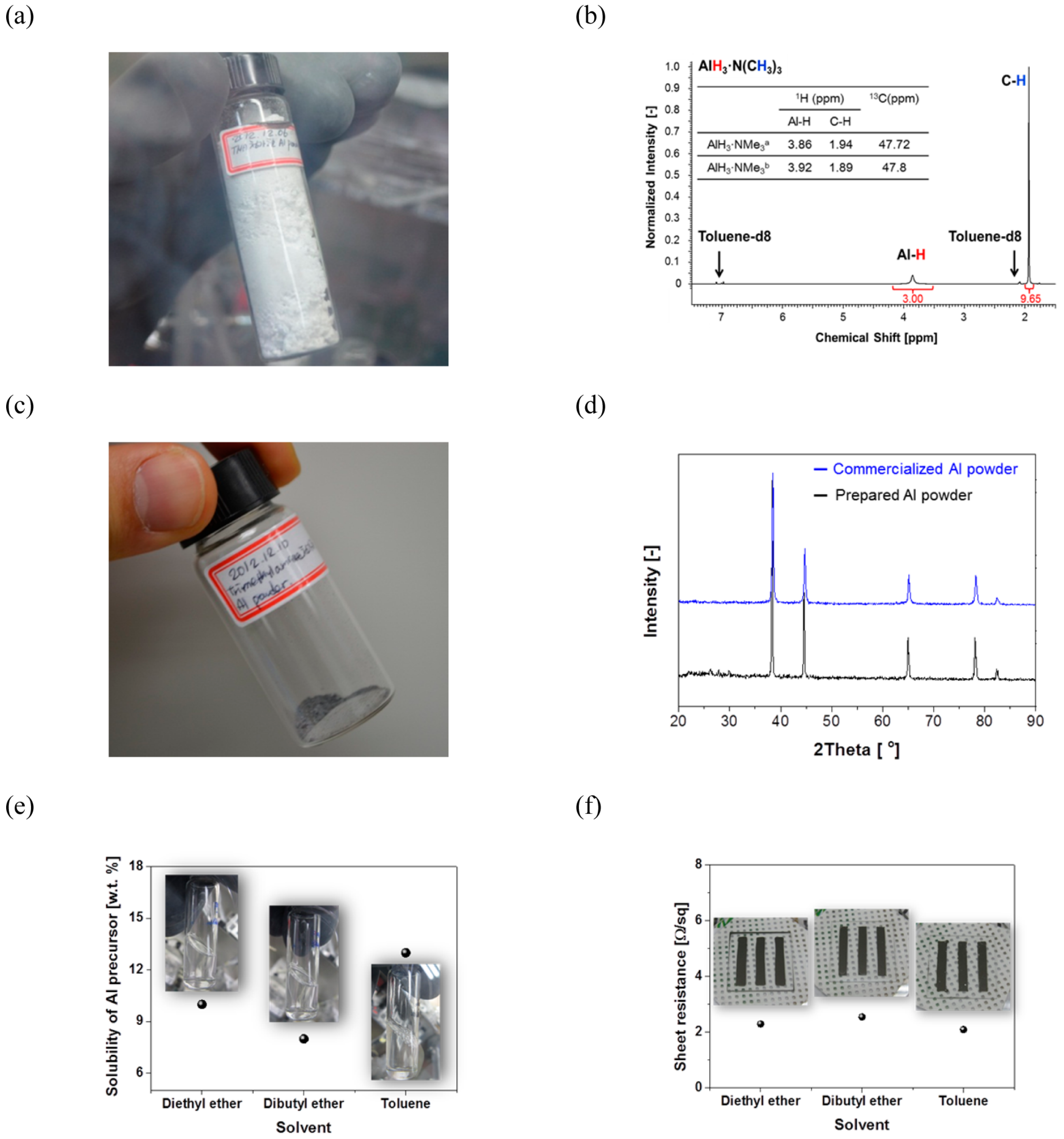


Figure 1. Mechanical endurance test of Al film on rigid and flexible substrates. (a) 3M Scotch tape test. (b) Bending test.

diameter. Therefore, for Al to be applied to the printed electronics, the development of novel methodologies to prepare Al ink without an oxidation problem is necessary. Furthermore, new ink materials as well as solution processes should be designed to prepare highly conductive Al features on substrates in a low-temperature environment.

Electroless-plating method, wherein the reduction agent (i.e., LiH or $LiAlH_4$) and the catalyst (i.e., Pd) were necessary, was utilized for preparation of Al films on rigid substrates;[15,16] however, this process is complicated and expensive since quire a long time is consumed for preparation of water-free Al ionic solution at inert and dry atmosphere. Furthermore, the electroless-plated Al film exhibits large sized Al grains, so that the prepared Al film exhibit the significant surface roughness. On the other hand, the methodology for high-quality Al films was recently suggested by Shen et al.,[17] which is the more simple solution process and further makes it possible to selectively deposit the local area. However, the preparation of patterned Al films should be performed on Pt/TiO_2 coated substrates, so that their method is regarded as a restrictive and expensive process. The first demonstration of the Al precursor solution of $AlH_3\{O(C_4H_9)_2\}$ and the processes for decomposing the precursor solution on a substrate was suggested by Lee et al.[11−14] to achieve the preparation of Al thin film with high conductivity in low-temperature surroundings. The suggested materials and methods successfully provided highly conductive Al film on rigid and flexible substrates at low temperatures (<150 °C). However, they still have the drawback of the relatively short lifetime of the Al precursor solutions, as discussed below. The precursor solution consists of $AlH_3\{O(C_4H_9)_2\}$ dissolved in dibutyl ether as a solvent, but the $AlH_3\{O(C_4H_9)_2\}$ is easily extracted as a solid from the



	^1H (ppm)		^{13}C(ppm)
	Al-H	C-H	
$AlH_3 \cdot NMe_3$[a]	3.86	1.94	47.72
$AlH_3 \cdot NMe_3$[b]	3.92	1.89	47.8

Figure 2. Prepared Al precursor and their feasibility in preparation of Al precursor ink for the solution processed highly conductive Al thin film electrodes. (a) Powder type $AlH_3\{N(CH_3)_3\}$. (b) NMR spectrum of powder (a) (inset is H, C, and Al chemical shifts measured for the $AlH_3\{N(CH_3)_3\}$ data). (c) Powders artificially decomposed from the $AlH_3\{N(CH_3)_3\}$. (d) XRD patterns of the decomposed powders and commercial Al powders. (e) Solubility of $AlH_3\{N(CH_3)_3\}$ powders in diethyl ether, dibutyl ether, and toluene (insets are Al precursor solutions prepared by fully solving the $AlH_3\{N(CH_3)_3\}$ powers in solvents). (f) Electrical sheet resistances of Al films prepared on sodalime glass substrates by a solution-stamping process using the Al precursor solution shown in part (e).

precursor solution due to its low solubility. Furthermore, the extracted $AlH_3\{O(C_4H_9)_2\}$ is crystallized in certain types of α-, β-, and γ-AlH_3 and subsequently decomposed into Al and H_2 due to its low activation energy for its decomposition.[11−14,18,19] This suggests that the previous development of the $AlH_3\{O(C_4H_9)_2\}$ solution lacks long-term sustainability and therefore may not be suitable for preparing an Al film with a uniform thickness and uniform electrical resistance. Therefore, in order to increase the long-term reliability to apply an Al precursor solution with a uniform AlH_3 concentration to the preparation of Al films with uniform electrical properties, it is essential to develop novel AlH_3 composites with stability levels superior to that of $AlH_3\{O(C_4H_9)_2\}$ and to store them without chemical degradation for a long shelf time.

In this study, therefore, we developed an innovative solution process for an Al precursor with long-term stability, as follows: (i) the preparation of powder-type AlH_3 composites with enhanced chemical stability, (ii) the storage of the powder-type

AlH_3 composites in low-temperature surroundings, and (iii) the preparation of an Al precursor ink by redissolving the stored powder in a solvent for the long-term use of AlH_3 composites without chemical degradation during the fabrication of Al thin film electrodes. Furthermore, the proposed method was experimentally confirmed to be very effective with regard to the long-term sustainability of Al precursor ink for solution-processed Al features with high electrical conductivity on both rigid and flexible substrates.

EXPERIMENTAL SECTION

Materials. $LiAlH_4$ (95%), $N(CH_3)_3{\cdot}HCl$ (98%), anhydrous diethyl ether (99.7%), anhydrous dibutyl ether (99.7%), and anhydrous toluene (99.8%) were puschased from Aldrich. All reagents and solvents were used as-received without further treatment.

Preparation of the Al Precursor Composite Powders $AlH_3\{N(CH_3)_3\}$. Scheme 1 shows the preparation procedure of Al precursor composite powders in detail. $LiAlH_4$ and $N(CH_3)_3{\cdot}HCl$ react rapidly and smoothly in ether at room temperature to produce $AlH_3\{N(CH_3)_3\}$ in good yield.[20] For preparation of $AlH_3\{N(CH_3)_3\}$ powders, 1:1 molar ratio of $LiAlH_4$ to $N(CH_3)_3{\cdot}HCl$ were mixed overnight in solvent of diethyl ether at room temperature. The clear solution, $AlH_3\{N(CH_3)_3\}$ solved in diethyl ether, was acquired by filtering the overnight reacted slurry type products. Furthermore, the prepared $AlH_3\{N(CH_3)_3\}$ was extracted as powder type materials redissolvable in solvents from the prepared clear solution by rotary evaporation process set at 100 rpm and 50 °C. The prepared $AlH_3\{N(CH_3)_3\}$ powders were stored at lower than ~5 °C for preventing their chemical decomposition.

Preparation of the Al Precursor Ink for Highly Conductive Al Thin Film. Al precursor ink was prepared by redissolving the as-prepared and chilly stored $AlH_3\{N(CH_3)_3\}$ powders in diethyl ether, dibutyl ether, and toluene, which are chemically stable and nonpolar solvents dissolving the solid phase of tertiary amine aluminum hydride (AlH_3NR_3) well.

Preparation of Highly Conductive Al Thin Film. Highly electrical conductive Al thin film was formed on rigid (soda lime glass) and flexible (PET and paper) substrates by a solution-stamping process with the solutions of the $AlH_3\{N(CH_3)_3\}$ powders. Detailed information on the solution-stamping process can be found in Supporting Information (SI) Figure S1 or our previous research.[11,12]

Characterization and Evaluation. NMR: The chemical structure of the prepared Al precursor powders was analyzed by NMR. The ^1H NMR spectrum of the Al precursor powders was acquired by an Agilent 400 MHz NMR instrument with toluene-d_8 as a NMR solvent. The NMR samples was prepared by dissolving 1 mg of Al precursor powders in 5 mL of toluene-d_8. The chemical shifts of ^1H NMR spectrum are referenced to the residual signal of toluene-d_8 singlet at 7.09 ppm. **XRD (X-ray diffractometer) analysis:** The crystal structure of the decomposed materials from the prepared Al precursor powders was analyzed with an X-ray diffractometer (XRD, Rigaku, D/Max 2200) with Cu K*α* radiation. **FE-SEM (field-emission scanning electron microscopy) observation of Al thin film:** Microstructures of surface and cross section of Al thin films were observed by a FE-SEM (Magellan 400). Especially, samples for observation of film cross section were prepared by focused ionized beam (FIB; Helios Nanolab 450 F1, FEI Co.) treatment of Al films on soda lime glass substrates. The FIB works with a highly focused gallium ion beam at 30 kV. **Electrical resistance measurements:** Electrical sheet resistances of Al films on substrates were measured by a four-point probe method (CMT-SR 1000N, Advanced Instrument Technology), and probe station method (model 5500, MS-Tech, Korea) was used to measure the linear electrical resistance. **Mechanical endurance test of Al films on substrates:** 3M Scotch tape (Figure 1a) and bending (Figure 1b) tests were performed to investigate the Al film adhesion to the substrate and the durability against the damage, such as scratching and peeling off. The tape test was carried out by strongly attaching 3M Scotch tape onto the Al film on the substrate and subsequently peeling off the tape. The bending test was performed at bending radii of 2, 5, 10, 20, 30, and 40 mm. For the bending test, electrical linear resistance was measured while the Al film formed on PET substrate was flat and bent and compared.

RESULTS AND DISCUSSION

Generally, ethers are significantly less than amines in terms of basicity. Hence, amines are stronger than ethers in terms of their ability to bond to AlH_3. Thus, we tried to prepare AlH_3

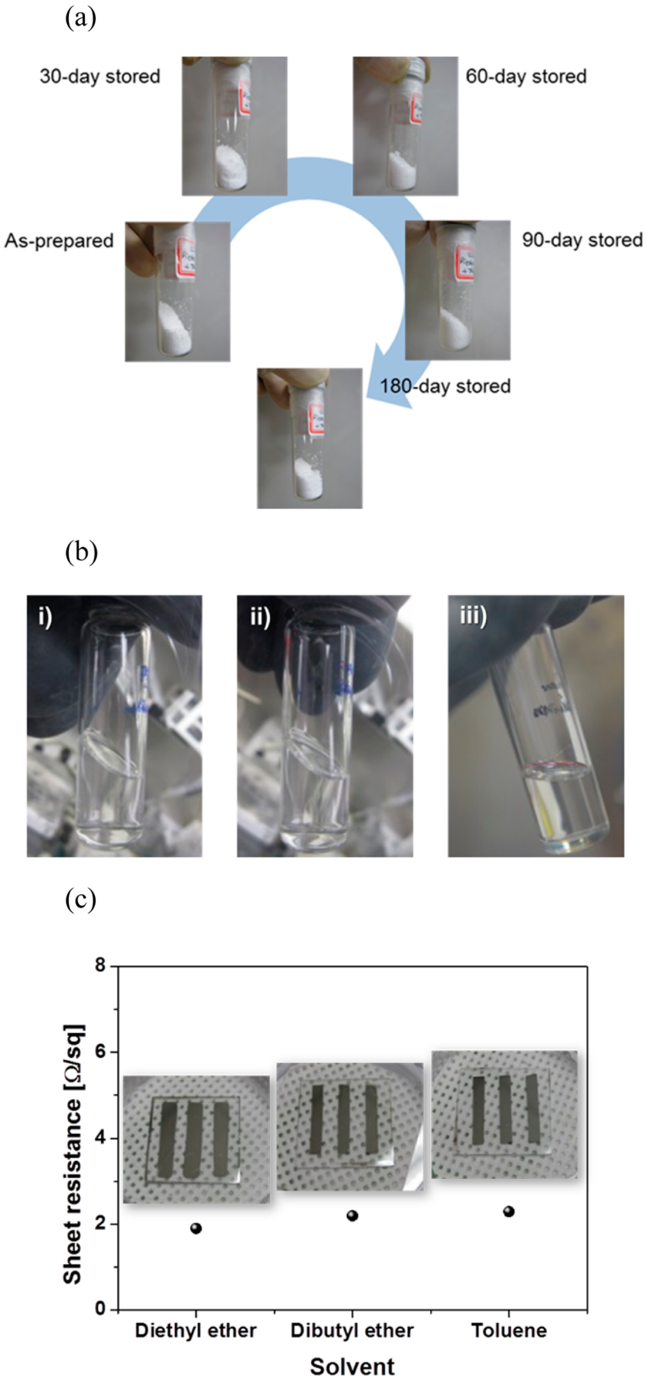


Figure 3. (a) As-prepared and 30−180-day stored $AlH_3\{N(CH_3)_3\}$ powders at ~5 °C. (b) Al precursor solutions prepared by fully solving the 180-day stored $AlH_3\{N(CH_3)_3\}$ powders in diethyl ether (i), dibutyl ether (ii), and toluene (iii). (c) Al thin films prepared by the Al precursor solutions shown in (b) and their electrical sheet resistance values.

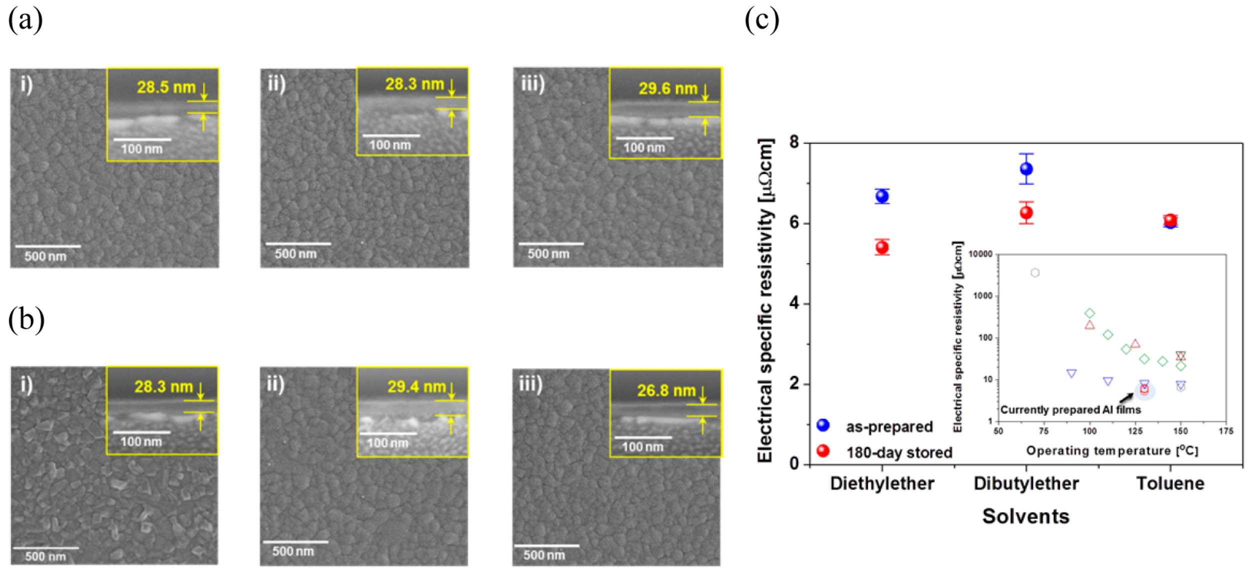


Figure 4. SEM surface and cross section (insets) images of Al films prepared using Al precursor solutions consisting of (a) the as-prepared and (b) 180-day stored $AlH_3\{N(CH_3)_3\}$ powders dissolved in (i) diethyl ether, (ii) dibutyl ether, (iii) toluene. (c) Their electrical specific resistivity (inset: comparison of Al films prepared in this research with previously reported samples; red circles, Al films prepared in current research; blue reverse triangles,[11] Al films prepared by $AlH_3\{O(C_4H_9)_2\}$; brown triangles[10] and green diamonds,[23] Ag films prepared by Ag colloid ink; gray hexagon,[24] Ag film prepared by Ag paste; and black reverse triangle,[25] Ag film prepared by Ag colloid ink).

aminates of $AlH_3\{N(CH_3)_3\}$, which is expected to be superior to AlH_3 etherates of $AlH_3\{O(C_4H_9)_2\}$ in terms of its chemical stability. Figure 2 shows digital pictures and the characterization of the prepared Al precursor powders used for the preparation of the Al precursor ink for the solution-processed highly conductive Al features. First, we characterized the AlH_3 composite powders prepared by the process described in Scheme 1. As shown in Figure 2a and b, the prepared powders consist of bright white granules experimentally confirmed to be $AlH_3\{N(CH_3)_3\}$ by a NMR analysis (Figure 2b). The comparison of the chemical NMR spectra for the prepared powders and the reference $AlH_3\{N(CH_3)_3\}$ reported in the literature[21] demonstrates that the chemical shifts for both powders are quite similar and that the ratio of the Al−H to C−H signal is quite close to 3:9, indicating that $AlH_3\{N(CH_3)_3\}$ was well formed during the stabilization step of the AlH_3 composite powders. In addition, the artificially decomposed materials from the prepared $AlH_3\{N(CH_3)_3\}$ powders are dark gray, which is in good agreement with the FCC crystal structure of pure aluminum in terms of color (Figure 2c) and the XRD pattern (Figure 2d), indicating that the prepared $AlH_3\{N(CH_3)_3\}$ powder is suitable for use in preparing an Al precursor ink used for the solution-processed highly conductive Al feature. The artificial decomposition of $AlH_3\{N(CH_3)_3\}$ powders was performed at ~130 °C for ~5 min in a chamber filled with catalyst fume. Next, for the preparation of the Al precursor ink with $AlH_3\{N(CH_3)_3\}$, the most appropriate solvent in which the $AlH_3\{N(CH_3)_3\}$ can be highly soluble must be selected. Parts e and f of Figure 2 respectively show the solubility levels of $AlH_3\{N(CH_3)_3\}$ powders in various solvents (diethyl ether, dibutyl ether, and toluene) and Al films formed on the surfaces of soda lime glass (SLG) substrates by a solution-stamping process with the solutions of the $AlH_3\{N(CH_3)_3\}$ powders. The maximum solubility of the $AlH_3\{N(CH_3)_3\}$ powders in the diethyl ether, dibutyl ether, and toluene solvents show relatively high values of 10, 8, and 13 wt %, respectively, demonstrating that preparations of very clear Al precursor solutions can be easily achieved by dissolving the $AlH_3\{N(CH_3)_3\}$ powders in various solvents. Contrary to the Ag or Au colloidal ink, no problematic agglomeration occurs because the $AlH_3\{N(CH_3)_3\}$ powders can be fully dissolved in the chosen solvents. Furthermore, it was experimentally confirmed that Al films with low electrical sheet resistance levels (<3 Ω/sq) were formed on the surfaces of the SLG substrates by the Al precursor solution in which $AlH_3\{N(CH_3)_3\}$ powders were fully dissolved. Therefore, $AlH_3\{N(CH_3)_3\}$ powders can be successfully utilized to prepare Al precursor ink for solution-processed highly conductive Al films on substrates.

AlH_3 is reported to decompose at ~165 °C.[22] However, the low Gibbs free energy for decomposition at room temperature makes it difficult to store AlH_3 for a long shelf life because it readily decomposes into Al and $1.5H_2$ at room temperature. This decomposition was also experimentally confirmed in this study (see SI Figure S2). In order to examine the influence of storage temperature, $AlH_3\{N(CH_3)_3\}$ powders stored in room temperature surroundings, refrigerator (set at ~5 °C), and freezer (set at ~−10 °C) were compared, showing that the chemical decomposition to some degree was observed only in $AlH_3\{N(CH_3)_3\}$ powders stored at room temperature. This comparison results are shown in SI Figure S3 in more detail. Therefore, the prepared $AlH_3\{N(CH_3)_3\}$ powders were stored in refrigerator for 180 days in an effort to keep them chemically stable for a long time as shown in Figure 3. While the chemical decomposition of $AlH_3\{N(CH_3)_3\}$ powders results in a color change from white to dark gray, no noticeable color changes were observed in all of the $AlH_3\{N(CH_3)_3\}$ powders stored in refrigerator for 30−180 days, as shown in Figure 3a, indicating that no chemical decomposition of $AlH_3\{N(CH_3)_3\}$ powders occurred during their storage in a refrigerator. After long-term storage confirmation of the Al precursor powder, we tried to prepare an Al precursor solution by redissolving the 180-day stored $AlH_3\{N(CH_3)_3\}$ powders in various solvents (diethyl ether, dibutylether, and toluene). As shown in Figure 3b, very

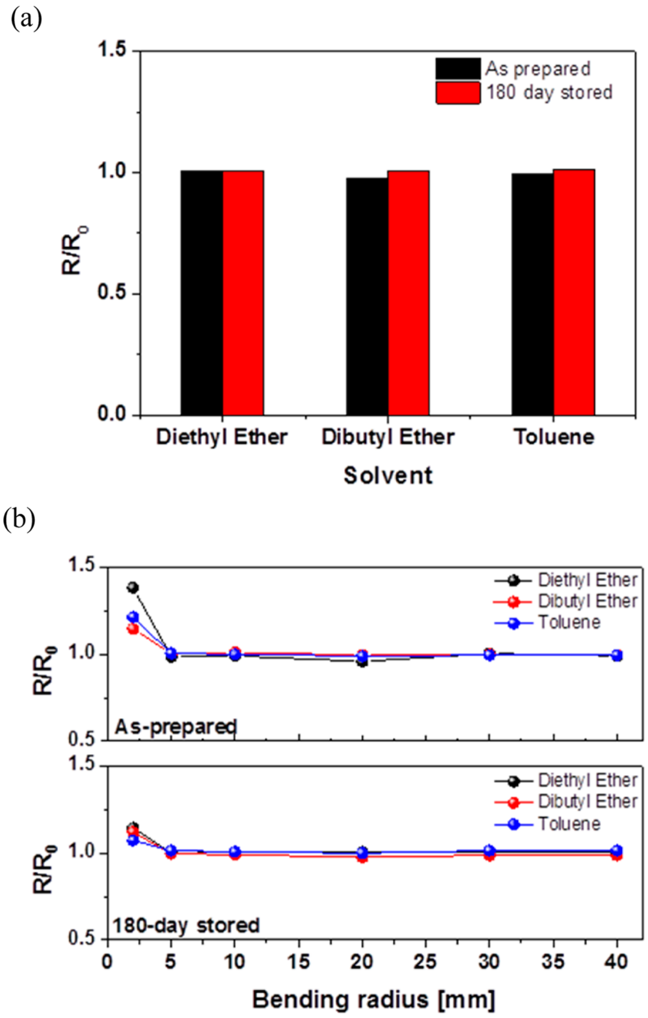


Figure 5. Mechanical endurances of Al films on PET substrates by the as-prepared and 180-day stored $AlH_3\{N(CH_3)_3\}$ powders solved in solvents. (a) Electrical resistance changes of Al films before and after Scotch tape adhesion test. (b) Electrical resistance changes of Al films on PET substrates under various bending radius.

clear Al precursor solutions were obtained, and no differences were visually detected between the precursor solutions with the as-prepared and 180-day stored $AlH_3\{N(CH_3)_3\}$ powders. Furthermore, it was also experimentally confirmed that Al films with electrical sheet resistance levels of 1.8−2.3 Ω/sq were successfully formed on SLG substrates by Al precursor solutions prepared from the 180-day stored $AlH_3\{N(CH_3)_3\}$ powders, as shown in Figure 3c.

Given that the electrical sheet resistances can vary with the thicknesses of the sheet, the electrical specific resistivity is more useful standard in comparisons of Al films fabricated by Al precursor ink with the as-prepared and 180-day stored $AlH_3\{N(CH_3)_3\}$ powders. Thus, we performed FE-SEM analyses of Al films formed on SLG substrates with the as-prepared (Figure 4a) and 180-day stored $AlH_3\{N(CH_3)_3\}$ powders (Figure 4b) redissolved in solvents (i, diethyl ether; ii, dibutyl ether; iii, toluene). From surface grain and cross-section SEM images, it was found that all of the prepared Al films consist of dense surface grains with a size range of 60−150 nm; moreover, they show very uniform thicknesses of 26−30 nm. Figure 4c shows the electrical specific resistivity of Al films prepared by all types of Al precursor solutions as determined by the electrical sheet resistances displayed in Figures 2f and 3c and their measured thicknesses. All of the Al features formed on SLG substrates by Al precursor ink with the as-prepared and 180-day stored $AlH_3\{N(CH_3)_3\}$ powder show electrical specific resistivity levels of 5.8−7.0 μΩ·cm, which are much lower than those (32−65 μΩ·cm) of Ag films prepared from colloidal inks consisting of Ag nanoparticles. Therefore, the low-temperature storage of $AlH_3\{N(CH_3)_3\}$ powders is a very efficient way to maintain the quality of the powders for longer times than several months and to prepare Al precursor ink for solution-processed highly conductive Al features on substrates as well.

Along with the excellent electrical properties, the mechanical stability under various external forces should be also guaranteed before applying the prepared Al films to flexible or wearable electronic devices applications. Thus, 3M Scotch tape and bending tests were also performed to investigate the degree of film adhesion to the substrate and durability against damage such as scratching and bending deformation. The Scotch tape did not peel off any of the Al films formed on the SLG substrates by Al precursor ink with the as-prepared and 180-day stored $AlH_3\{N(CH_3)_3\}$ powders. Thus, no significant degradation of the electrical sheet resistance was detected before and after the tape tests (Figure 5a). Moreover, the results of the bending tests of the Al films formed on PET substrates are shown in Figure 5b. Although the bending tests were performed at bending radii of 2−40 mm, the electrical sheet

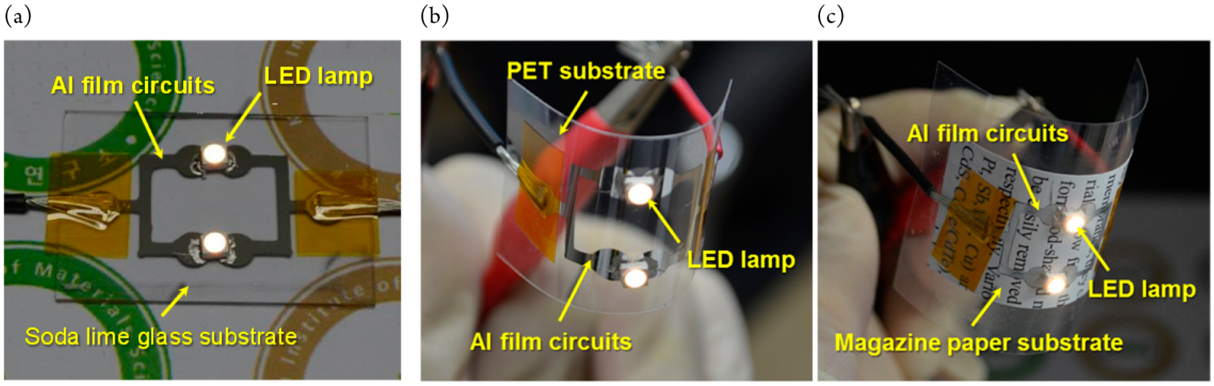


Figure 6. Digital pictures of LED lamps on the Al line pattern films prepared by the 180-day stored $AlH_3\{N(CH_3)_3\}$ powders solved in solvents (a, diethyl ether; b, dibutyl ether; c, toluene). (a) Flashed on LED lamps connected to the flat line patterned Al films formed on SLG, (b) bent line patterned Al films on PET, and (c) paper substrates.

resistance started to increase only at bending radii of less than 5 mm with all types of Al precursor solutions. At a bending radius of 5 mm, the Al film formed on the flexible substrate was seriously bent as shown in Figure 1b, indicating that Al films can strongly adhere to flexible substrates with all types of Al precursor inks. Overall, it was confirmed that long-term stored $AlH_3\{N(CH_3)_3\}$ powders can be used in the preparation of Al precursor ink for the fabrications of Al films with excellent electrical and mechanical properties on rigid and flexible substrates.

Finally, Figure 6 demonstrates the applicability of our solution-processable Al to actual electronics devices on various substrates fabricated from Al precursor inks with 180-day stored $AlH_3\{N(CH_3)_3\}$ powders. Figure 6, parts a, b, and c, shows LED lamps mounted onto patterned Al films formed on SLG, PET, and paper substrates, respectively. The LED lamps in all cases flashed under DC bias, even working with bent Al films on flexible PET and paper substrates. Reaction of Al with oxygen is so active that a thin Al oxide layer (3−10 nm) always exists on the surface of Al features. Once the Al oxide layers are formed on the surface of Al features, the oxidations of Al features do not show further serious progress. This is because the thin native Al oxide layers are so dense that oxygen hardly penetrates into the oxide layers to induce further oxidation even at atmospheric surroundings. Thus, the solution processed Al features show long-term electrical stability even in the atmospheric surroundings. SI Figure S4 shows the long-term electrical functionality measurement after its initial fabrication and 9-month storage in the air environment. Therefore, the Al films prepared by Al precursor inks with $AlH_3\{N(CH_3)_3\}$ powders are sufficiently feasible for rigid and flexible electronics devices.

CONCLUSIONS

In conclusion, we suggest a unique method for the preparation of the Al precursor $AlH_3\{N(CH_3)_3\}$ with feasible long-term physical and chemical stability levels. To fabricate the Al precursor ink, the prepared $AlH_3\{N(CH_3)_3\}$ powder can be simply redissolved in diethyl ether, dibutyl ether, or toluene. The prepared Al precursor inks are readily applicable to the preparation of highly conductive Al films with excellent mechanical endurance levels against external deformation on substrates. Furthermore, low-temperature storage was found to be an effective means of avoiding the chemical degradation of the $AlH_3\{N(CH_3)_3\}$ powders with which Al films were formed on both rigid and flexible substrates by Al precursor inks. Even $AlH_3\{N(CH_3)_3\}$ powders stored for six months are applicable to preparation of Al precursor ink for fabricating Al films with excellent and uniform electrical and mechanical properties. Therefore, we expect that the proposed method, consisting of three steps, (i) the preparation of Al precursor powders, (ii) the low-temperature storage of the prepared Al precursor powders, and (iii) the redissolution of the Al precursor powders in a solvent, will pave the way for the preparation of electrically and mechanically uniform Al films on various substrates via solution-based processes. In addition, we are expecting that the long-term stored $AlH_3\{N(CH_3)_3\}$ powders will be very applicable to Al precursor ink for various printing and coating devices.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Solution-stamping process for preparation of highly conductive Al thin film on substrate, Gibbs free energy for chemical decomposition of AlH_3, aluminum produced by chemical decomposition of Al precursor solution at room temperature, device consisting of long-term sustainable Al film circuits. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Email: hyelee@kims.re.kr.

Notes

The authors declare no competing financial interest.

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