

ARTICLE

Self-reducible copper complex inks with aminediol and OH-based solvent for highly conductive copper film by calcination at low temperature under an air atmosphere

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Akihiro Yabuki^{*a}, Takuhiro Sakaguchi^b, Indra Wahyudhin Fathona^c, and Ji Ha Lee^{*a}

A simple fabrication of copper conductive film was accomplished in one step at low temperature under an air atmosphere. The strategy for solving the problem was the use of both aminediol and OH-based solvent for self-reducible copper complex inks. The complex ink consisted of copper formate, aminediol, and various OH-based solvents calcinated at various temperatures, which resulted in conductive copper film via rapid calcination at low temperature. The ratio of copper formate, aminediol, and OH-based solvent in complex inks was optimized for higher conductive copper film. Copper film from complex ink with a ratio of 1 (copper formate) : 2.2 (aminediol) : 1.8 (diol solvent) was rapidly calcined at 180 °C under an air atmosphere and showed approximately 15 $\mu\Omega$ cm, which is approximately 10 times that of bulk copper. The combination of aminediol and OH-based solvent inhibited the oxidation of the copper surface via adsorption. The developed process is applicable to conductive circuits, resistors, and capacitors in the form of oxide films for use as printable electronics fabricated under an air atmosphere.

Introduction

Conductive metal inks are being widely used to produce conductive films on flexible substrates intended for application to printed/wearable electronic products.^{1,2,3,4,5,6} Printable processes using the metal inks are expected for novel manufacturing processes which increases the energy consumption compared to conventional processes. To offset this increased consumption, copper ink is touted as an effective candidate for the development of flexible electronic devices that can offer advantages such as being easy to handle, low-cost, and amenable to production via highly efficient solar energy.^{5,7,8,9,10,11} Nevertheless, copper is limited by a tendency toward oxidation under air. The processes required to produce conductive copper films are as follows: (1) low-temperature calcination below 200 °C; (2) high conductivity at a volume resistivity of 10 $\mu\Omega$ cm; and, (3) manufacture under an air atmosphere.

Several groups have attempted to prepare copper film with satisfactory values and have succeeded in synthesizing copper film either under air or at low temperature.^{12,13,14,15,16} Yonezawa et al., have reported a low-temperature sintering process for

copper film with Cu²⁺-alkanolamine metallacycle compounds.¹² Their process used a sintering temperature of approximately 100 °C, and their copper film has shown resistivity to 900 $\mu\Omega$ cm. Kang et al., proposed a sintering process using a laser under an air atmosphere.¹³ They used a laser with a 532 nm wavelength and a 5 W maximum power output. They used various levels of laser power and applied them under an air atmosphere to create 21 $\mu\Omega$ cm copper film. Kawasaki et al., have succeeded in fabricating conductive copper films via low-temperature sintering under air.¹⁴ Conductive copper films on flexible polymer substrates have been successfully demonstrated under air atmosphere sintering at low temperatures (less than 150 °C). Oxalic acid was added to prevent the oxidation of the Cu during sintering. The Cu films showed a minimum resistivity of 55 $\mu\Omega$ cm when sintered under air at 150 °C for a very short period of 10 s. These results, however, failed to achieve the high conductivity that was required.

Over the past decade, we attempted to develop copper films with high electrical conductivity using copper-amine complex inks by controlling the various conditions at lower temperatures.¹⁷ Copper film with low volume resistivity (5 $\mu\Omega$ cm) was developed under a N₂ atmosphere by selecting the proper amine and determining the calcination conditions.¹⁸ The synthesis of copper film under an air atmosphere in our previous work showed that an effective volume resistivity of the film could be achieved through mixing with aminediol.¹⁹ Volume resistivity of 300 $\mu\Omega$ cm, however, was high compared with film synthesized under a N₂ atmosphere, but still failed to achieve the required level.

The key technology obtained from the corresponding research was a method for the prevention of an attack by oxygen via the use of the OH species in aminediol. In the

^a Chemical Engineering Program, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-hiroshima, 739-8527, Japan.

^b Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-hiroshima, 739-8527, Japan

^c Physics Engineering Department, Electrical Engineering Faculty, Telkom University Terusan Telekomunikasi, Dayeuh Kolot Bandung, 40257, Indonesia

* Corresponding author. Tel/fax: +81 82 424 7852

E-mail address: ayabuki@hiroshima-u.ac.jp (A. Yabuki), leejiha@hiroshima-u.ac.jp (J. H. Lee)

present research, to improve the volume resistivity of the copper film, we added an OH-based solvent to the complex ink with aminediol. The strategy was to inhibit the oxidation of the copper surface after calcination. Various types of OH-based solvents were mixed in the complex inks to improve the volume resistivity of the copper film. The ratio of copper formate, aminediol and OH-based solvent was optimized to obtain highly conductive copper film. To accomplish anti-oxidation, we proposed a mechanism that combined aminediol and OH-based solvent.

Experimental

Copper formate tetrahydrate (Kanto Chemical Co., Inc.) was dried at 80 °C for 6 h to obtain anhydrous copper formate (Cuf). Then, 3-Dimethylamino-1,2-propanediol (b.p. 216–217 °C, Kanto Chemical Co., Inc.) was selected as an OH-based amine that could be used to produce complex ink. OH-based solvent was added to the complex ink to improve its anti-oxidation properties of the ink. Three types of OH-based solvents (Tokyo Chemical Industry Co., Ltd.) were selected: 2-ethyl-1,3-hexanediol (b.p. 243 °C); 1,3-propanediol (b.p. 211–217 °C); and, 1-propanol (b.p. 97–98 °C). The ratio of Cuf, amine, and solvent was set as 1: 2–2.2 : 0–2 (Fig. 1).

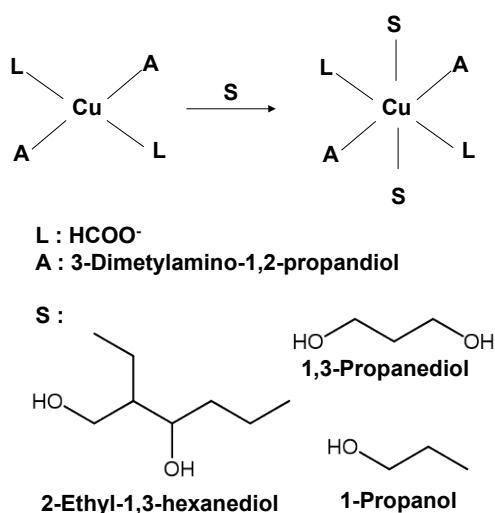


Fig. 1 The structure of the copper complex ink with aminediol and OH-based solvent.

The prepared complex ink was coated onto a cleaned glass substrate using a masking tape that was approximately 15 μm in thickness. The coated substrate was placed directly onto the heated hot plate of a bell jar type vacuum oven (BV-001, Shibata Scientific Co., Ltd.) under an air atmosphere. The temperature was held at 140 to 190 °C for 30 min, and the substrate was removed for cooling under an air atmosphere.^{19,20}

The electrical conductivity of the prepared copper film was measured using a four-point probe (MCP-T600, Loresta-GP, Mitsubishi Chemical Corp.). The thickness of the films was measured via observation of their cross-sections using an optical micrograph (VHX-100, Keyence Corp.). The morphology of the films was observed

using field-emission scanning electron microscopy (FE-SEM, JSM6340F, JOEL Ltd.) at an accelerated voltage of 20 kV. In addition, the surfaces of the films were analyzed via energy dispersive X-ray fluorescence spectrometry (EDS). The crystallite phases of the prepared films were measured via X-ray diffractometer (XRD, RINT 2200V, Rigaku-Denki Corp.).

Results and discussion

The volume resistivity of copper films prepared from complex inks of Cuf, amine, and three types of OH-based solvents at various holding temperatures by rapid calcination appears in Fig. 2. The ratio of Cuf, amine and OH-based solvent was 1:2:2. The copper film calcined at 150 °C showed no electrical conductivity, because the thermal decomposition of the copper complex did not proceed. The volume resistivity of the copper film calcined at 190 °C could not be determined due to an uneven surface. When the holding temperature was increased from 160 to 180 °C, we confirmed a tendency for all OH-based solvents to show a decrease in the volume resistivity of the copper film. The volume resistivity of the copper films calcined from complex ink with 1,3-propanediol (Fig. 2b) and 1-propanol (Fig. 2c) was the lowest, and had similar values at 180 °C. When the surface of the films was compared, the film prepared from the ink with 1,3-propanediol was brown in color, although the surface was not uniform and many pores were observed having been generated by the evaporation of produced gas (Fig. 3). The color change was related to the boiling point of the solvents and calcination temperature, that is, 1-propanol (b.p. 97–98 °C) was easily evaporated during calcination, however, 1,3-propanediol (b.p. 211–217 °C) was slowly evaporated, which was prevented oxidation of the copper surface. Calcination at 180 °C accelerated both thermal decomposition and oxidation, but thermal decomposition was dominant at 180 °C. This result showed that both 1-propanol and 1,3-propanediol could prevent oxidation of the inner structure of the film during thermal decomposition. However, 1,3-propanediol possessed the characteristics required to prevent surface oxidation following thermal decomposition. Thus, the complex ink composed of 1,3-propanediol was further investigated.

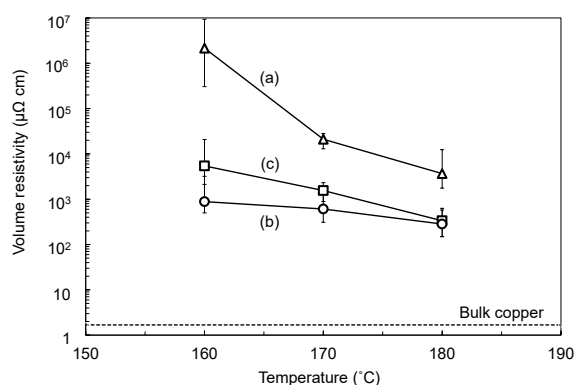


Fig. 2 The volume resistivity of copper film prepared at various holding temperatures from copper-amine complex ink with (a) 2-ethyl-1,3-hexanediol, (b) 1,3-propanediol, and (c) 1-propanol. The ratio of copper formate, amine and solvent was 1:2:2.

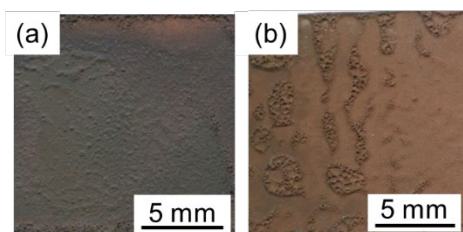


Fig. 3 The surface of the copper film prepared from copper-amine complex ink with (a) 1-propanol and (b) 1,3-propanediol at 180 °C. The ratio of copper formate, amine and solvent was 1:2:2.

The optimal molar ratio of amine used to prepare copper film with low resistivity under an air atmosphere was investigated. The volume resistivities of copper film prepared from an ink complex of Cuf, amine, and 1,3-propanediol at different amine ratios under various temperatures appear in Fig. 4. The ratio of amine to Cuf was varied from 1.8 to 3. The ratio of 1,3-propanediol to Cuf was fixed at 1.8. The lowest value was confirmed for a ratio of amine to Cuf of 2.2 at 180 °C. Due to the structure of a copper complex that is formed from mainly a 4 or 6 coordination, an amine to Cuf ratio of 2 was expected to be appropriate. However, since the complexing did not reach 100% in the actual complex formation, a ratio of 2.2 appeared to form a stable copper complex.

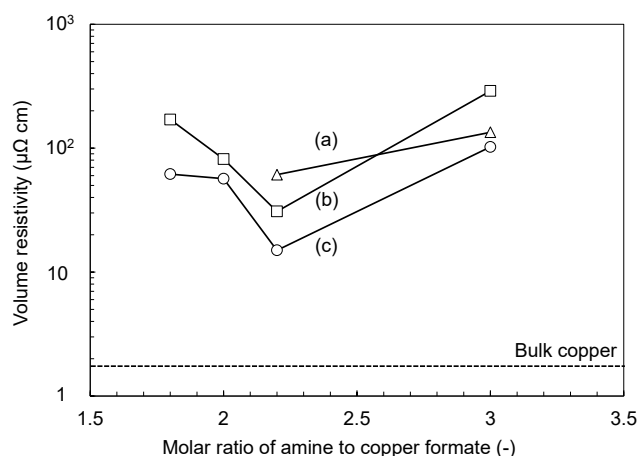


Fig. 4 The volume resistivities of copper films prepared from copper complex ink of copper formate, amine and 1,3-propanediol at different ratios of amine and at various holding temperatures of (a) 160 °C, (b) 170 °C, and (c) 180 °C. The ratio of 1,3-propanediol to Cuf was fixed at 1.8.

The ratio of 1,3-propanediol was further optimized. The volume resistivities of copper film calcined from complex inks with various molar ratios of 1,3-propanediol to Cuf at various holding temperatures appear in Fig. 5. The ratio of amine to Cuf was fixed at 2.2. The volume resistivity of copper film prepared at 160 °C was almost constant, although it was largely increased at a ratio of 2.0. On the other hand, the volume resistivities of copper film prepared at 170 °C showed the minimum value at solvent ratios of 1.0 and 1.8. The volume resistivities of copper film prepared at 180 °C showed a pattern similar to that at 170 °C, but resulted in the lowest values for all ranges of solvent ratios, and the lowest value was 15 $\mu\Omega$ cm for a

ratio of 1.8. Copper film prepared from complex ink with no solvent shows a resistivity of 200 $\mu\Omega$ cm, whereas copper film prepared from ink with 1,3-propanediol at a ratio of 1.8 showed 15 $\mu\Omega$ cm, which amounts to one tenth or less. Thus, we confirmed that an optimum addition of 1,3-propanediol results in copper film with lower resistivity. The volume resistivity tended to decrease until the proportion of 1,3-propanediol was increased from 0 to 1. This suggested that the 1,3-propanediol required a ratio of at least 1 to be structurally coordinated with the copper formate complex, since 1,3-propanediol has OHs at both end terminals, as shown in Fig. 1. The sharp decrease in volume resistivity at a ratio of 1.8 meant that under these conditions the copper complex expected in Fig. 1 was forming. However, an excess addition of 1,3-propanediol increased the resistivity.

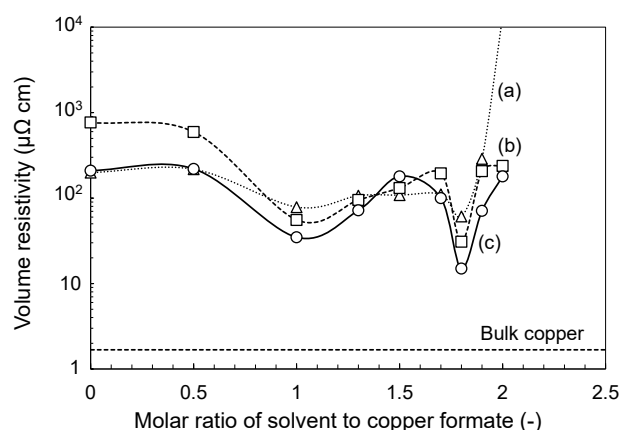


Fig. 5 The volume resistivity of copper film calcined from complex inks with different molar ratios of 1,3-propanediol solvent to Cuf at various holding temperatures of (a) 160 °C, (b) 170 °C, and (c) 180 °C. The ratio of amine to Cuf was fixed at 2.2.

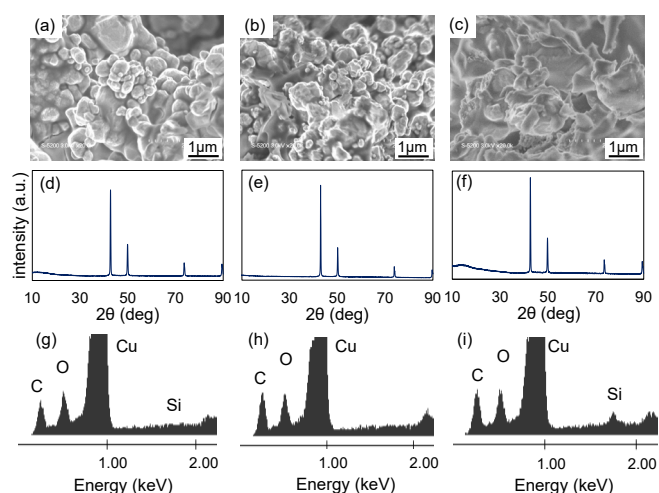


Fig. 6 SEM images, XRD patterns and EDS analysis of copper films prepared from complex ink with different ratios of 1,3-propanediol to copper formate: 0 (a, d, g); 1.8 (b, e, h); and, 2.0 (g, h, i). The ratio of amine to copper formate was fixed at 2.2.

The SEM images, XRD pattern, and EDS analysis of copper films prepared from complex inks with 1,3-propanediol ratios to Cuf of 0, 1.8, and 2 at 180 °C are shown in Fig. 6. The ratio of amine to Cuf was fixed at 2.2. At 1,3-propanediol ratios of 0 and 1.8, the films consisted of nanoparticles that were 100 nm in size, and some of the particles were connected (Fig. 6a and 6b). At a 1,3-propanediol ratio of 2.0 the film seemed to consist of flakes (Fig. 6c).

The results of XRD showed three peaks near 45, 50, and 72 in 2 θ (Fig. 6d, 6e and 6f), which resulted from the crystal structure of copper particles in the film (JCPDS NO 04-0836). EDS analysis, however, showed peaks of C and O in the films at various ratios of 1,3-propanediol. In the film with no 1,3-propanediol (Fig. 6g), the O peaks were slightly larger than the C peaks, but in the film with 1,3-propanediol the O peaks approximated those of the C peaks (Fig. 6h and 6i). This showed that 1,3-propanediol inhibited the oxidation of the particle surface. This analysis shows that copper film could be prepared from complex ink via rapid calcination and that oxidation of the surface is prevented via the use of an OH-based solvent. Also, lower volume resistivity of the copper film was accomplished by optimizing the ratio of Cuf, amine and OH-based solvent. Fig. 3 illustrates this result by showing the color of the copper surface for two types of film. The high resistivity of the copper film with a 2.0 ratio of 1,3-propanediol was due to the flake-like morphology.

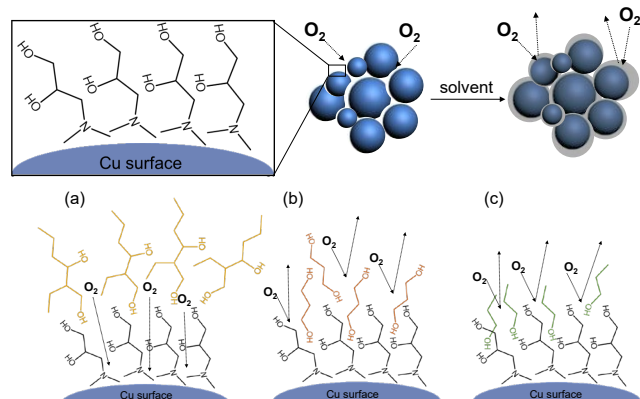


Fig. 7 Mechanism for preventing the oxidation of copper particles by adsorbed amine and OH-based solvent: (a) 2-ethyl-1,3-hexanediol, (b) 1,3-propanediol, and (c) 1-propanol.

The low-volume resistivity of copper film prepared at 180 °C was mainly caused by a decrease in the surface oxidation of copper particles via the use of an OH-based solvent and rapid calcination. The EDS results in Fig. 7 confirm that it was the OH-based solvents that mainly prevented the oxidation of the copper. These results suggest that the volume resistivity of the copper film was reduced through treatment with a simple solvent when amine was adsorbed onto the copper surface, as previously reported.¹⁹ In addition, the copper surface was covered with an OH-based solvent that enhanced the prevention of oxidation. Fig. 2 confirms that the values of the volume resistivity were different depending on the type of OH-based solvent that was used. The difference in the volume resistivity represented a correlation between the type of OH-based solvent and the structure of the solvent itself. When the OH-based solvent was added to the copper-amine treated state, (1) there was hydrogen bonding with the amine solvent on the copper surface, (2) adsorption

occurred on the copper surface, and (3) the boiling point became an issue. The steric nature of 2-ethyl-1,3-hexanediol creates difficulty in inducing hydrogen bonding near the copper surface (Fig. 7a). On the other hand, linear solvent structures such as 1-propanol and 1,3-propanediol could easily be expected to be present between copper particles, as shown in Figs. 7b and 7c. As a result, this could prevent copper oxidation via protection from oxygen. In the present study, 1,3-propanediol did not show a significant difference in volume resistivity at 160 to 180 °C, whereas 1-propanol showed about a 10-fold difference in volume resistivity at those temperatures, as shown in Fig. 2. Thus, both aminediol and OH-based solvent inhibited the oxidation of the surface of copper after calcination. The developed process could be applied as conductive circuits, resistors, and capacitors in the form of oxide films for use as printable electronics fabricated under an air atmosphere.

Conclusions

Self-reducible copper complex ink consisting of copper formate, aminediol and various OH-based solvents was calcinated at various temperatures under an air atmosphere, which resulted in conductive copper film produced via simple rapid calcination at low temperature under an air atmosphere. As an OH-based solvent, 1,3-propanediol with two OHs at the end terminal was capable of preventing oxidation. With the optimized ratio (1 (copper formate) : 2.2 (aminediol) : 1.8 (diol solvent)) the copper film calcined from complex ink at 180 °C by rapid calcination under an air atmosphere showed approximately 10 $\mu\Omega$ cm. Both aminediol and the OH-based solvent inhibited the oxidation of the copper surface after calcination. The developed process could be applied as conductive circuits, resistors, and capacitors in the form of oxide films for use as printable electronics fabricated under an air atmosphere.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1. M.-C. Daniel and D. Astruc, *Chemical reviews*, 2004, **104**, 293-346.
2. J. N. Freitas, A. S. Gonçalves and A. F. Nogueira, *Nanoscale*, 2014, **6**, 6371-6397.
3. T. T. Nge, M. Nogi and K. Suganuma, *Journal of Materials Chemistry C*, 2013, **1**, 5235-5243.
4. N. Toshima and T. Yonezawa, *New Journal of Chemistry*, 1998, **22**, 1179-1201.
5. W. Yang, E. J. W. List-Kratochvil and C. Wang, *Journal of Materials Chemistry C*, 2019, **7**, 15098-15117.
6. D.-H. Shin, S. Woo, H. Yem, M. Cha, S. Cho, M. Kang, S. Jeong, Y. Kim, K. Kang and Y. Piao, *ACS applied materials & interfaces*, 2014, **6**, 3312-3319.
7. V. Abhinav K, V. K. Rao R, P. S. Karthik and S. P. Singh, *RSC Advances*, 2015, **5**, 63985-64030.
8. Y.-H. Choi, J. Lee, S. J. Kim, D.-H. Yeon and Y. Byun, *Journal of Materials Chemistry*, 2012, **22**, 3624-3631.

9. Y. Keriti, R. Brahim, Y. Gabes, S. Kaci and M. Trari, *Solar Energy*, 2020, **206**, 787-792.
10. W. Xu and T. Wang, *Langmuir*, 2017, **33**, 82-90.
11. C. Paquet, T. Lacelle, X. Liu, B. Deore, A. J. Kell, S. Lafrenière and P. R. L. Malenfant, *Nanoscale*, 2018, **10**, 6911-6921.
12. T. Yonezawa, H. Tsukamoto, Y. Yong, M. T. Nguyen and M. Matsubara, *RSC Advances*, 2016, **6**, 12048-12052.
13. J. H. Yu, K.-T. Kang, J. Y. Hwang, S.-H. Lee and H. Kang, *International Journal of Precision Engineering and Manufacturing*, 2014, **15**, 1051-1054.
14. M. Kanzaki, Y. Kawaguchi and H. Kawasaki, *ACS applied materials & interfaces*, 2017, **9**, 20852-20858.
15. S. Cho, Z. Yin, Y.-k. Ahn, Y. Piao, J. Yoo and Y. S. Kim, *Journal of Materials Chemistry C*, 2016, **4**, 10740-10746.
16. Y. Yong, M. T. Nguyen, H. Tsukamoto, M. Matsubara, Y.-C. Liao and T. Yonezawa, *Scientific reports*, 2017, **7**, 45150.
17. A. Yabuki, N. Arriffin and M. Yanase, *Thin Solid Films*, 2011, **519**, 6530-6533.
18. A. Yabuki and S. Tanaka, *Materials Research Bulletin*, 2012, **47**, 4107-4111.
19. A. Yabuki, Y. Tachibana and I. W. Fathona, *Materials Chemistry and Physics*, 2014, **148**, 299-304.
20. A. Yabuki and S. Tanaka, *Materials Research Bulletin*, 2011, **46**, 2323-2327.

Graphic Abstract

