Performances of screen-printing silver thick films: Rheology, morphology, mechanical and electronic properties

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Highlights

- Powder dispersion correlates well with screen-printing thick film performances.
- Rheological fingerprints can be utilized to fathom the powder dispersion state.
- Good polymer-powder interactions in the paste ensure good powder dispersion.
- Time-dependent gel-like viscoelastic features are found with optimum silver pastes.
- The size and shape of functional powder affect the dispersion and film performances.

Abstract

Numerous recent applications with inorganic solar cells and energy storage electrodes make use of silver pastes through processes like screen-printing to fabricate fine conductive lines for electron conducting purpose. To date, however, there have been few studies that systematically revealed the properties of the silver paste in relation to the mechanical and electronic performances of screen-printing thick films. In this work, the rheological properties of a series of model silver pastes made of silver powders of varying size (0.9, 1.3, and 1.5 μm) and shape (irregular and spherical) were explored, and the results were systematically correlated with the morphological feature (scanning electron microscopy, SEM) and mechanical (peeling test) and electronic (transmission line method, TLM) performances of screen-printing dried or sintered thick films. We provided evidence of generally intimate correlations between the powder dispersion state in silver pastes—which is shown to be well captured by the rheological protocols employed herein—and the performances of screen-printing thick films. Overall, this study suggests the powder dispersion state and the associated phase behavior of a paste sample can significantly impact not only the morphological and electronic but also mechanical performances of screen-printing thick films, and, in future perspectives, a proper combination of silver powders of different sizes and even shapes could help reconcile quality and stability of an optimum silver paste.

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1. Introduction

Metal pastes are conventionally important suspension materials
that have found widespread applications in ceramics [1,2], solid oxide fuel cell [3–8], and inorganic solar cell [9,10] industries. A typical metal paste consists of the functional powder and an organic vehicle, which is often composed of polymeric binder, surfactant and solvent to provide suitable rheological properties [4–6,11–18] and dispersion state [11,19–24] for processing and quality-control purposes. In practice, the ability to precisely characterize the paste properties in relation to the performances of subsequently fabricated thick films is crucial. To date, however, there have been few studies that systematically unveiled the powder dispersion state in a paste sample and, furthermore, delved into the mechanical and electronic performances of the subsequently produced thick films [11,20,21,23]. Bridging these material properties is, evidently, of great importance both scientifically and technologically.

In prior work on low-content silver pastes, we showed the dispersion state of the functional powder may be fattened by specially designated rheological features—the so-called rheological fingerprints [25]. Specifically, the (nonlinear) transient viscosity growth in start-up of steady-shear experiment along with the (linear) viscoelastic response in dynamic oscillation experiment had been utilized to identify a peculiar phase evolution similar to typical sol-gel transition, suggestive of significantly promoted sample elasticity attributable to a surfactant-aided enhanced polymer-powder interaction and the thus improved powder dispersion state. Herein, for a new series of model paste samples made of silver powders of varying size and shape, we endeavor to relate the paste properties to the performances of screen-printing thick films through a combination of rheological measurements, scanning electron microscopy (SEM) imaging, and mechanical and electronic characterizations. It is shown there are generally intuitive and scanning electron microscopy (SEM) imaging, and mechanical and electronic characterizations for a series of experimental results of prior thick films. Afterward, the powder dispersion states of dried and sintered thick films, as viewed from SEM morphologies, are examined in conjunction with the corresponding structural development within the paste samples, and therefore the rheological characterizations introduced herein seem to serve as a convenient and powerful means for this purpose.

This paper is organized as follows: we first describe the materials, sample preparations, and rheological experiments for a series of model paste samples, along with post-assessments of their screen-printing thick films. Afterward, the powder dispersion states of dried and sintered thick films, as viewed from SEM morphologies, are examined in conjunction with the corresponding structural development within the paste samples, and therefore the rheological characterizations introduced herein seem to serve as a convenient and powerful means for this purpose.

2. Experimental

2.1. Materials

Silver powders labeled as T silver (ThinTech Materials Technology Co., Kaohsiung, Taiwan), D silver (DOWA Electronics Materials Co., Ltd., Japan), and S silver (Mitsu Kinzoku, Japan) were used in this work, as shown by the SEM (S4800-U, Hitachi, Tokyo, Japan) images in Fig. 1. Unless noted otherwise, the organic vehicle consists of polymer binder, surfactant, and solvent. Ethyl cellulose (EC) (Ethocel™ STD 300) polymeric binder was provided by Dow Chemical Co. (Shanghai, China) with an ethoxyl content of 48.0–49.5% by weight. The solvent used, α-terpineol, bears high purity (>95%) and low volatility and was purchased from Taiwan Tekho Fine Chem Co. (Taipei, Taiwan). Stearic acid (SA, >95%) was purchased from Sigma-Aldrich (US). Bismuth-based glass frit added for sintering purpose was purchased from Esoar Materials Technology Co. (Taiwan).

2.2. Paste preparations

The compositions of four model paste samples are summarized in Table 1. Detailed procedures of the sample preparation were as follows: polymer binder (EC) and surfactant (SA) were first dissolved in α-terpineol at 80 °C with the aid of a mixer (ARV-930 TWin, Thinky, Tokyo, Japan) for 2 h. The organic vehicle so prepared was then cooled down at room temperature and further mixed with the silver powder and the glass frit to produce the paste samples. In the last step, the mixture was mildly stirred for about 10 min prior to the treatment with a three-roll mill (80E, EXAKT Advanced Technologies GmbH, Norderstedt, Germany) at room temperature. To promote the uniformity of the pastes and for the purpose of deagglomeration, the back and front roller gaps were consecutively adjusted in the following fashion: 50(μm)/50(μm), 50/40, 40/30, 30/20, 20/15 in totally five mixing circles. To scrutinize the effects of aging on the powder dispersion state and the corresponding structural development within the paste samples, the prepared samples were stored at room temperature for various aging times prior to simultaneous rheological measurements and thick film fabrications and characterizations.

2.3. Rheological measurements

Rheological measurements were conducted using a controlled stress rheometer (MCR 500, Anton Paar GmbH, Graz, Austria) and a cone-and-plate fixture (diameter = 50 mm, cone angle = 1°) equipped with Peltier temperature controller. For comparison, some of the paste samples have been doubly tested in a different rheometer (DHR-2, TA Instruments, New Castle, DE) using both cone-and-plate and parallel-plate fixtures, showing consistent trends as with the data reported herein. The detailed procedure of sample loading was as follows: the sample was first loaded on the bottom plate at a higher temperature 40 °C for 10 min to assist the removal of air bubble. The temperature was then reduced to 25 °C, while waiting for another 10 min for the material to attain thermal equilibrium. The upper cone was subsequently lowered to the measured position with a gap size of 53 μm, and settled for 10 min to reduce any memory effect that might result from the loading procedure. Finally, the initial state was created by pre-shearing the sample at a shear rate 0.1 s⁻¹ for 2 min to promote the homogeneity of the loaded sample, followed by 2 min of resting period. Thixotropy of the paste samples was noted to be insignificant for the low solid content (~7 vol%) presently investigated, and therefore the subsequent measurements were found to be insensitive to the details of sample loading or other pre-treatments.

A series of rheological measurements were conducted including oscillation and rotation experiments, and the detailed procedures can be found elsewhere [25]. The present study, however, is focused on exploring the relationship between paste samples with various aging times and the corresponding powder dispersion states, as well as the performances of their screen-printing thick films.

2.4. Thick film fabrication and post-assessments

To fabricate thick films, green lines of 4.5 mm in width were deposited onto multiple crystalline (mc)-Si wafers through a commercial screen printer (EKRA X5 STS, ASYS Group GmbH, Germany) with 200 meshes. The printing wet films were dried at 250 °C for about 10 min before the SEM images were taken. The
that, for silver powders bearing similar mean size, the one with a more regular, spherical shape (i.e., P-EC8SA3SG) does not necessarily lead to a better dispersion state, contrary to the expectation from the sole consideration of packing theory. Finally, it is of interest to note that the two samples made of silver powders of different size (and size distribution) and shape yield quite similar thick film morphologies, as shown in Fig. 2(b) and (c).

The morphological features of the sintered films exhibit similar trends, as can be seen in Fig. 3. Namely, a better powder dispersion in dried printing film generally leads to more uniform (and compact) grain growth in the sintered film. Overall, the SEM images of dried and sintered films reveal interestingly contrasting powder dispersion states for four paste samples made of the same vehicle agent (except for P-EC8TG) Yet with silver powders of varying size and shape. In a later discussion, we show that the powder dispersion state in a silver paste can be well captured by the corresponding (time-evolving) rheological features, which shed light on the effects of the powder attribute and the interactions with the vehicle agent.

The performances of a sintered thick film are often evaluated by electrical and mechanical characterizations, respectively. In principle, the electrical resistance should be as low as possible, while the mechanical strength as high as possible. On the basis of these criteria, it is clear that the results summarized in Fig. 4(a) and (b) basically conform to the superiority in the dispersion state as discussed previously with Figs. 2 and 3. Namely, the thick films fabricated by using the paste samples P-EC8SA3TG and P-EC8SA3DG that exhibited fine powder dispersion display relatively low electrical resistance and high peeling strength. In particular, the P-EC8SA3DG sample made of the smallest, uniformly spherical powder appears to achieve the best overall performance.

Noticing a generally intimate correlation between the powder dispersion state and the mechanical and electronic performances of a thick film, one is curious to know the features of the pristine paste samples that have possibly predetermined all these thick film properties of practical interest. Next, we discuss rheological characterizations of the paste samples that shed light on the (time-evolving) structural development leading to distinct powder dispersion states as have been noted above.

sintered thick films were later produced using a belt furnace. The electrical resistance of sintered films was measured using transmission line method (TLM) with four-point probe method (Digit Precision Multimeters, 8846A, Fluke, Everett, US). The corresponding adhesion strength was estimated in peeling test through solar module laminator (LS-RX2000, MOGRL, Taiwan) with a 90-angle peel fixture.

3. Results and discussion

3.1. Morphologies and performances of screen-printing thick films

Thick films fabricated by screen-printing various silver pastes may be judged first by their morphological features in the SEM imaging, because the dispersion state of the functional powders that has a major impact on the mechanical and electronic properties of the sintered films [20,21,23] can be clearly revealed. In the following discussion, the organic vehicle used to prepare silver paste samples remains the same—except for one (i.e., P-EC8TG) which was produced without the surfactant SA for contrasting purpose—so that the sole impact of the silver powder can be better discerned. The composition of this organic vehicle, in fact, has been somewhat optimized to enhance the polymer-powder interactions deemed crucial to confer a silver paste the desirable dispersion state and overall sample elasticity; see detailed discussion in prior work [25].

Fig. 2 compares the dried (green) film morphologies for four different paste samples with various aging times. At present, we focus on the effects of silver powder and sample composition, deferring the effect of aging to a later discussion. It can be seen that while the P-EC8SA3TG and P-EC8SA3DG samples yield a fine dispersion state of the silver powders after screen-printing and drying, the other samples (i.e., P-EC8TG and P-EC8SA3SG) produce thick films with an appreciable amount of large pores indicative of pronounced powder aggregation. Clearly, the dispersion state is not solely determined by the size or shape of silver powders. For instance, comparing Fig. 2(a) and (b) for two paste samples made of the same silver powder reveals distinct degrees of powder aggregation, evidently more pronounced for the one without SA (i.e., P-EC8TG). Moreover, the results shown in Fig. 2(b) and (d) indicate

### Table 1

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>EC300 (wt%)</th>
<th>n-Terpineol (wt%)</th>
<th>Stearic acid (wt%)</th>
<th>Silver powder (wt%)</th>
<th>Glass powder (wt%)</th>
</tr>
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<tr>
<td>P-EC8TG</td>
<td>4</td>
<td>46.0</td>
<td>–</td>
<td>47 (T)</td>
<td>3</td>
</tr>
<tr>
<td>P-EC8SA3TG</td>
<td>4</td>
<td>44.5</td>
<td>1.5</td>
<td>47 (T)</td>
<td>3</td>
</tr>
<tr>
<td>P-EC8SA3DG</td>
<td>4</td>
<td>44.5</td>
<td>1.5</td>
<td>47 (D)</td>
<td>3</td>
</tr>
<tr>
<td>P-EC8SA3SG</td>
<td>4</td>
<td>44.5</td>
<td>1.5</td>
<td>47 (S)</td>
<td>3</td>
</tr>
</tbody>
</table>

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Fig. 1. SEM images of three different silver powders used in this work: (a) T silver, (b) D silver, and (c) S silver with mean particle diameters of 1.3 μm, 0.9 μm, and 1.5 μm, respectively. Note that whereas D and S silvers are relatively monodisperse in powder size and assume a regular, spherical shape, the T silver is mostly composed of irregular frits.
Fig. 2. SEM images contrasting the screen-printing thick films after drying at 250 °C, produced from (a) P-EC8TG, (b) P-EC8SA3TG, (c) P-EC8SA3DG and (d) P-EC8SA3SG at different aging times.

Fig. 3. SEM images contrasting the screen-printing thick films after sintering, produced from (a) P-EC8TG, (b) P-EC8SA3TG, (c) P-EC8SA3DG and (d) P-EC8SA3SG at different aging times.
transient viscosity growth after startup of a steady shearing at various rates. With prolonged aging, one observed a drastic and somewhat peculiar growth of the transient viscosity at low shear rates for EC8SA3DG (Fig. 6(c)) and, in particular, P-EC8SA3TG (Fig. 6(b)). In contrast, the other paste samples display little (Fig. 6(d)) or no (Fig. 6(a)) such behavior, and the overall responses quite resemble those of entangled polymer liquids as might be expected when polymer-polymer interaction remains poor and, hence, the polymer entanglement would dominate the rheological response; see more detailed discussion in prior work [25].

In conjunction with the SEM images shown in Figs. 2 and 3, it seems that a prominent enhancement in paste elasticity as has been noted in Figs. 5 and 6 may be correlated with an improved dispersion state in screen-printing dried and sintered thick films, which in turn leads to generally promoted thick film performances in view of electrical resistance and mechanical strength as shown in Fig. 4. The results help confirm a previous assertion that the pronounced transient viscosity growth in the rotation experiment, along with a gel-like behavior as noted in the oscillation experiment, was indicative of a better powder dispersion state arising from the formation of loosely packed (fractal) aggregates ready to bridge with each other and progressively percolate to form a continuous network [25]. In contrast, when a similar phenomenon was absent as with the cases of P-EC8SA3SG and P-EC8TG, large, compact aggregates prevail being unable to effectively bridge themselves given only a low solid content.

Given that Figs. 5 and 6 showed notable aging-time dependent behavior, it is of interest to examine the impact on thick film properties. First, the SEM images in Figs. 2 and 3 show little change in the powder dispersion state with aging time, in part because the images provide only the top-view morphological feature. On the other hand, Fig. 4 shows the electrical resistance is more responsive to the effect of aging as compared with the mechanical strength. As we noted earlier, the silver paste made of uniformly spherical and smaller silver powder, P-EC8SA3DG, leads to the best overall performance among all four. Therefore, an examination of the corresponding rheological features in Figs. 5 and 6 suggests that a rapid yet moderate growth in the sample elasticity could be of an optimum one, in comparison with the other sample, P-EC8SA3TG, which exhibits truly remarkable elasticity growth. For the latter, in fact, the paste viscosity eventually turned so large that the printing process becomes notably hindered or even prohibited. Thus, there appears to be an imperative need to reconcile quality and stability as far as a practical silver paste is concerned, as we discuss further below.

During the entire period of aging as has been attempted in this work, the P-EC8SA3SG sample made of uniformly spherical yet slightly larger silver powder, as compared with P-EC8SA3DG discussed above, has displayed a surprisingly slight (or slow) tendency toward the aforementioned elasticity development. The central implication is, hence, that a paste sample made of mixing silver powders that are relatively uniform in shape yet of varying size could help fine-tune quality and stability of an optimum silver paste that would best meet the requirements of screen-printing thick films, especially when sample storage is of additional concern.

4. Conclusions

We have examined a series of model silver pastes made of silver powders of varying size and shape along with a common, somewhat optimized, organic vehicle, as well as the screen-printing thick films fabricated from them. Focus is on a systematic revelation of the correlations between the rheological features of the paste samples—which have been shown to be an excellent means to fathom the powder dispersion state—and the morphological,
mechanical, and electronic properties of screen-printing dried or sintered thick films. The central finding was that, whenever a prominent growth of the paste elasticity has been noticed simultaneously in both (nonlinear) rotation and (linear) oscillation experiments, one observed a promoted powder dispersion state (mainly through SEM images) in both dried and sintered films, along with a general enhancement in thick film performances as characterized by electrical and mechanical measurements. As suggested in prior work [25], this phenomenon may be understood as surfactant-aided, enhanced polymer-powder interactions that make possible the formation of loosely packed powder fractals and progressively percolated network, as contrasted with the formation of bulky aggregates in the other cases that contribute to the porous structures as were evident in the SEM images of dried and sintered thick films. To our knowledge, this is among the few studies that have clearly established the general correlations between silver paste compositions/properties, the powder dispersion state, and the thick film performances.

Regarding the apparent effects of the size and shape of the silver powders under investigation, it was found that the paste sample made of uniformly spherical and smaller silver powder (i.e., P-EC8SA3DG) leads to the best overall performance, predictable also from the attendant rheological features which demonstrate a rapid yet moderate growth in the sample elasticity. Surprisingly, however, the counterpart paste sample (i.e., P-EC8SA3SG) made of slightly larger spherical powder (cf. 0.9 μm and 1.5 μm) exhibited a
Fig. 6. Transient viscosity growth during startup of steady shearing at various shear rates for paste samples (a) P-EC8TG, (b) P-EC8SA3TG, (c) P-EC8SA3DG, and (d) P-EC8SA3SG at different aging times; the inset plots show the detailed profile.
rather slow pace of elasticity growth and, consequently, yielded only poor powder dispersion and notably inferior thick film performances within the time span of this experiment. To reconcile the practical requirements of having a paste sample that is stable during long-term storage and, on the other hand, is sufficiently fast to develop the desirable structure and dispersion state, the central implication appears to be that certain combinations of spherical silver powders of varying size could lead to optimum paste samples. In this respect, the time-resolved rheological features as employed herein seem to provide an excellent means to speed up the identification process.

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