

Title	Development of low temperature curable Cu inks with high conductivity and reliability for printed flexible electronics
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Osaka University

Abstract of Thesis

Name (李 万里)	
Title	Development of low temperature curable Cu inks with high conductivity and reliability for printed flexible electronics (プリントフレキシブルエレクトロニクスのための高導電かつ高信頼性な低温焼結Cuインクの開発)
<p>Abstract of Thesis</p> <p>Printable and flexible electronics have attracted much attention because of their eco-friendly manufacturing processes and unconventional features such as light-weight, bendable, and foldable. With the market expansion, to develop cheap Cu inks instead of expensive Ag/Au nanoparticles inks becomes increasingly inevitable. However, the high preparation cost and oxidation of Cu nanoparticles as well as the poor stability of printed Cu patterns are insurmountable obstacles for their practical applications. This dissertation provides three strategies: using submicron Cu particles instead of Cu nanoparticles, utilizing intense pulsed light (IPL) sintering, and introducing anti-oxidation Ag element, to address the oxidation problem of Cu inks and improve the conductivity and reliability of printed Cu patterns, enabling them to replace or partly replace the noble Ag and Au inks in the application of printable and flexible electronics.</p> <p>At first, the concept that using in-situ formed fresh Cu nanoparticles to help sinter the submicron Cu particles has proved feasible by the developed submicron Cu particle/Cu complex inks. During the low temperature heat treatment of 140 ° C, fresh Cu nanoparticles decomposed from Cu complex can attach to the submicron Cu particles and activate their surface, which contributes to sintering and neck-growth among these submicron Cu particles to achieve conductive pathways. With the reinforcement of IPL sintering, the microstructure of printed Cu patterns become denser and robust, and a resistivity below $5.8 \times 10^{-6} \Omega \cdot \text{cm}$ is successfully achieved, which is superior to those obtained from Cu nanoparticle inks. Importantly, the method opens a new way for making highly reliable and highly conductive Cu patterns with large Cu particles instead of nanoparticles, which can largely decrease the cost and enhance the application of Cu inks for flexible electronic devices.</p> <p>In order to improve the oxidation resistance of printed Cu patterns, printable and flexible Cu-Ag alloy patterns with high conductivity and ultrahigh oxidation resistance were successfully fabricated by using a newly developed Cu particle/Ag complex ink and employing a two-step sintering method. The Cu particle/Ag complex ink firstly transforms into a Cu-Ag nanoparticle core-shell structure under a low temperature of 140 ° C in air and then further transforms into Cu-Ag alloy under IPL sintering. It was revealed that the obtained Cu-Ag alloy patterns have a bulk-like microstructure and show a very low resistivity of $3.4 \times 10^{-6} \Omega \cdot \text{cm}$ (50 % of the bulk conductivity of Cu). Most importantly, it was clearly demonstrated that the Cu-Ag alloy has a special core-shell structure with a Cu-rich phase in the core and an Ag-rich phase in the shell, showing high stability even in air at 180 ° C.</p> <p>Finally, for printing electronics on heat-sensitive PET or paper substrates, Cu-Ag complex inks were put forward to fabricate highly oxidation-resistant and conductive patterns at a low temperature below 100 ° C. The inks show an obvious self-catalyzed characteristic due to the in-situ formation of fresh metal nanoparticles which promote rapid decomposition and sintering of the inks at a low temperature below 100 ° C. The temperature is 40-60 ° C lower than those of general Cu complex inks and 100-120 ° C lower than those of general Cu/Ag particle inks. Highly conductive Cu-Ag patterns of $2.8 \times 10^{-5} \Omega \cdot \text{cm}$ and $6.4 \times 10^{-5} \Omega \cdot \text{cm}$ had been easily realized at 100 ° C and 80 ° C, respectively. In addition, the printed Cu-based patterns not only show high oxidation resistance at high temperatures of up to 140 ° C but also show excellent stability at high humidity of 85 % because of the very uniform Cu-Ag hybrid structure. The printable patterns exhibit great potential application in various wearable devices fabricated on textiles, papers, and other heat-sensitive substrates.</p> <p>In the dissertation, the results confirm that developing novel Cu inks with anti-oxidation property, and corresponding curing methods can greatly improve the conductivity and reliability of printed Cu patterns, enabling them to be acceptable in various printed electronics.</p>	

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨		
<p>今日、印刷技術によるエレクトロニクス製造技術が、魅力的な軽量フレキシブル性、折り曲げ性、廃棄物が少ない環境調和性、あるいは、低コストなどの特徴から注目されている。その実現には、安価な銅インク技術の確立が欠かせない。銅インクの開発では、銅粒子合成と印刷配線プロセスにおける酸化の防止に加え、配線形成後の酸化防止も大きな課題になる。本論文では、安価なサブミクロンサイズの銅粒子を出発原料とし、これらの酸化の課題を解決する低温焼結が可能な銅インクの開発と各種特性の評価を行い、以下の結果を得ている。</p> <ol style="list-style-type: none"> 1. サブミクロン銅粒子とギ酸銅塩を混合インクとすることで、140℃の窒素雰囲気中で低温焼成配線形成が可能になる。ギ酸銅塩は、この温度で全て分解し銅ナノ粒子を形成し、サブミクロン銅粒子の焼結に寄与する。さらに、フラッシュランプによる強い可視光照射により、ポリエチレンテレフタレート（PET）フィルム基板上で $5.8 \times 10^{-6} \Omega \cdot \text{cm}$ の低い体積抵抗率が得られる。 2. サブミクロン銅粒子とケトカルボン酸銀塩を混合インクとすることで、140℃の窒素雰囲気中で低温焼成配線形成が可能になる。ケトカルボン酸銀塩は100℃以下から銀ナノ粒子の形成を開始し、140℃では完全に銅粒子表面に銀ナノ粒子のコート層を形成する。さらに、フラッシュランプによる強い可視光照射することにより銀ナノ粒子表面層は溶融状態となり配線の密度が向上し、ポリイミドフィルム基板上で $3.48 \times 10^{-6} \Omega \cdot \text{cm}$ の低い体積抵抗率が得られる。銀量が10%程度を越えることで、この配線は180℃の大気中暴露においても優れた耐酸化性を示す。 3. ギ酸銅とケトカルボン酸銀塩の混合インクでは、100℃以下から銀ナノ粒子が形成し始め、さらに、ギ酸銅からの銅ナノ粒子の形成も低温化され、120℃以下の温度範囲で優れた配線形成が可能になる。この低温化によってPETフィルム基板や紙基板の上に形成した配線は優れた密着性を実現し、100℃において $2.8 \times 10^{-5} \Omega \cdot \text{cm}$ の体積抵抗率が得られる。この配線は、140℃までの耐酸化性と85℃/85%RHの高温高湿に対する耐性を示す。 <p>以上のように、本論文はフレキシブルエレクトロニクスの配線材料として魅力的な低抵抗配線の低温形成を実現しその配線形成メカニズムを解明し、しかも形成された配線の優れた耐酸化性を証明している。よって本論文は博士論文として価値あるものと認める。</p>		