银纳米线网络的高有序排列及其图案化设计

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摘要 银纳米线的高有序排列及图案化, 是制备柔性触控感知单元结构的关键步骤, 也是银纳米线透明导电薄膜实际应用的最具挑战性的难题之一. 传统的银纳米线有序化具有涂布速度慢、流体动力小、有序化程度不高等缺点. 本研究使用0.4 wt%超细银纳米线(直径20 nm)的乙醇溶液在快涂布速度下(60 mm/s)制备了有序化程度高达0.82的银纳米线透明导电薄膜. 银纳米线网络的超高有序化归因于毛细管作用力和流体动力的大幅度增加. 在有序化银纳米线网络结构的基础上, 利用常规光刻法和湿法刻蚀制备导电通道, 通道宽度范围为20~500 μm , 精度高达99%以上, 为可在拉伸电极中的实际应用提供了参考.

关键词 银纳米线, 透明导电薄膜, 有序排列, 图案化

透明导电电极在光电器件中应用十分广泛, 例如柔性太阳能电池、柔性触摸屏和显示屏等^[1~4]. 目前用来制备透明导电电极最常见的材料是氧化铟锡(ITO), 但由于ITO材料成本很高, 而且又硬又脆, 应用十分有限^[5,6]. 作为最有希望替代ITO的一种新型材料, 银纳米线(AgNWs)与石墨烯^[7~11]、碳纳米管^[11~13]、导电聚合物^[14,15]等相比, 其透光性和导电性更佳^[16~18]. 而且, AgNW网络可通过棒涂^[19~21]、旋涂^[22,23]或喷涂^[23~25]等方法直接制得, 成本低, 方法简便. 但一般的AgNW网络都是随机分布的, 往往会存在分布不均匀、表面粗糙度大、AgNWs容易缠绕在一起、AgNWs之间结电阻大等问题^[18,26].

针对上述问题, 研究者采用在AgNW墨水中添加微量有机物^[27]、在表面添加高分子聚合物涂层^[28]、机械压制^[18,29]以及热退火^[30]等方法. 但这些方法工艺流程复杂且效果不理想. 对此, Ko研究组^[31]提出了一种新的方法, 通过调整AgNWs的排布方向, 使之沿着同一个方向排列, 从而得到有序化AgNW网络, 其结点排

布也会变得均匀有序化, 所制得的透明导电薄膜(TCFs)方阻小且均匀, 表面光滑, 粗糙度小.

如表S1所示, 尽管通过掠入射喷涂的方法可以得到有序化程度很高的AgNW网络, 但其均匀性很差, 除了喷涂中心区域之外其他区域有序化程度都不高, 导致其透过率和方阻的均匀性不佳^[32~34]. 所以在实际应用中, 该方法并不适合推广. 还有一些研究小组分别采用毛细管辅助流体组件^[35]、刷涂^[36]、电流体力学印刷^[37]等方法, 均未得到有序化程度高且均匀性能好的AgNW TCFs. 而后, 很多研究组用棒涂法制备有序化AgNW TCFs, 得到的AgNW网络虽然均匀性好, 有序化程度较高, 但仍存在很大的提升空间^[31,38~41]. 为此, 我们通过改进AgNW清洗方法和棒涂法来制备有序化程度超高的交叉有序化AgNW TCFs. 同时, 可以通过在AgNW墨水中掺杂微量分散剂与流平剂, 保证墨水的均匀稳定性, 然后利用大型涂布机大规模制备均匀稳定的有序化AgNW TCFs.

然而, 有序化AgNW TCFs在显示设备中的应用有

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限,大多数显示器需要同时存在导电与非导电区域,因此,需要用图案化来解决这个问题,其图案化的精度直接决定了所制器件的性能高低^[42,43]。图案化的方法也有很多,比如丝网印刷^[44,45],通过应用蚀刻掩模版进行化学蚀刻^[46]等。然而,这些方法存在分辨率低、刻蚀区域与非刻蚀区域光学性能差异大导致肉眼可见等缺点^[47,48]。为了避免出现这种问题,改进了刻蚀步骤,使刻蚀前后AgNW TCFs透过率和雾度几乎不变。

在本研究中,制备了有序化程度超高的AgNW TCFs,并在其基础上做了简单的图案化。为此,通过改进AgNWs的动态搅拌清洗方法^[49]和Meyer棒涂方法,大幅度提高了有序化所需的毛细管力和流体动力,所制备的AgNW TCF的有序化程度高达0.82。还改进了光刻法和湿法刻蚀,制备了20~500 μm 宽的导电通道,其精度高达99%以上,刻蚀前后透过率的变化仅为0.04%,雾度变化率仅为-0.12%。

1 实验方法

(i) 实验试剂与耗材。乙醇(ET)购自国药化学试剂有限公司。聚赖氨酸(PLL)购自武汉千润生物工程有限公司。光刻胶AZ4620和显影液AZ400K购自苏州汶颢微流技术有限公司。3-甲氧基丙酸甲酯(MMP)和次氯酸钠(NaClO , 活性氯浓度为0.052 mg/mL)购自上海阿拉丁生化技术有限公司。醋酸(CH_3COOH)购自上海凌峰化学试剂有限公司。除 NaClO 外的所有化学试剂均为分析纯试剂。滤膜(孔径为8 μm)购自天台中力过滤设备厂有限公司。聚对苯二甲酸乙二醇酯(PET, 膜厚为125 μm)购自康德新复合材料集团股份有限公司。

(ii) AgNWs的纯化方法。将60 mL AgNW原液倒入带有滤膜(孔径为8 μm)的纯化装置中,用无水乙醇稀释至300 mL。六孔搅拌桨的搅拌速度设定为900 r/min。在清洗过程中,将乙醇慢慢滴入纯化装置中,以保持溶液恒定体积,共清洗40 min。清洗过后先进行一次正压过滤,然后加入36 mL聚乙烯吡咯烷酮(PVP, 0.5 wt%, 分子量为55000),摇晃均匀后再进行一次正压过滤。

(iii) 交叉有序化AgNW网络的制备。将纯化后的AgNWs(直径20 nm, 长度30 μm)均匀分散在不同溶剂(无水乙醇、去离子水、无水乙醇与去离子水体积比为1:1的混合溶液)中,分别配成不同的浓度(0.1 wt%~0.6 wt%)。PET基材分别在去离子水和乙醇中超声清洗5 min,然后用紫外臭氧处理30 min。用混匀仪以8000 r/min的速度将40 μL PLL水溶液(0.1 wt%)旋涂到

PET基材上。使用自动涂布机以不同的涂布速度(50~180 mm/s)在PLL/PET基底上制备有序化的AgNW TCFs。为了制备交叉有序化的AgNW阵列,在溶剂完全干燥后,立刻在单方向有序化的AgNW/PET基底上以垂直于预对准方向再次进行涂膜。

(iv) 超细AgNW导电通道的制备。将1 mL AZ4620/MMP溶液(体积比1:1)以7000 r/min的速度旋涂到交叉有序化的AgNW薄膜上。然后将其置于100°C加热板上加热不同时间(30~120 s),再利用掩模版将其暴露于不同曝光剂量(140~8064 mJ/cm^2)的紫外线(~365 nm)中,并用AZ400K溶液显影不同时间(3~8 s)。将显影后的AgNW薄膜浸入中性 NaClO 基蚀刻剂(活性氯的浓度为0.28 wt%)中不同时间(10~180 s)。经过化学蚀刻处理后,用乙醇溶液浸泡90 s去除AgNW薄膜上残留的光刻胶。

(v) 表征方法。用光学显微镜(OM, Axio Lab. A1)、扫描电子显微镜(SEM, Nova NanoSEM 450)和透射电子显微镜(TEM, FEI Talos F200S)表征产物的形态。用空白参比或用紫外线处理的PET作为参比,用紫外可见近红外光谱仪(Lambda 7500)在室温下测量TCF的透过率和雾度。使用四点探针法(RST-9)测量TCF的薄层电阻。用表面张力计(SFZL-A2)测量表面张力。25°C下,在黏度计(NDJ-5S)上获得黏度测量值。

2 结果与讨论

2.1 有序化AgNW TCFs的制备

根据已报道的涂膜法,我们用OSP-03涂膜棒在PET基底上以恒定的速度进行有序化TCFs的制备^[31,50-53]。如图1所示,未涂覆区域的AgNWs排列杂乱无章,毫无规律。OSP-03涂膜棒上的凹槽宽度仅为18 μm ,而AgNWs的最小长度约20 μm ,刮涂时,AgNWs会与涂膜棒上的螺纹发生碰撞,导致转向,直至能通过凹槽为止,从而得到预有序化的AgNW网络。

湿膜边缘溶剂的蒸发会引起毛细管作用力的变化,毛细管作用力 F_s 可定义为

$$F_s \approx 2\pi r\gamma, \quad (1)$$

其中, r 为AgNW的半径, γ 为墨水的表面张力^[31,39]。我们所制备的AgNWs的半径约为10 nm,墨水的表面张力为25.19 mN/m,计算所得毛细管作用力约为1.58 nN。AgNWs未完全对齐时,倾斜的AgNWs会使弯月面变

图1 (网络版彩色)有序化AgNW网络的制备原理示意图
Figure 1 (Color online) Schematic illustration of preparing aligned AgNW networks

形,导致两侧的动态接触角(θ_1 、 θ_2)大小不同,因此两侧的毛细管作用力的垂直分量不同,使AgNWs的另一端向完全对齐的方向移动,直至完全对齐($\theta_1 = \theta_2$)。

在涂膜过程中,还有两种比较重要的作用力,其一是流体动力,其二是摩擦阻力。流体动力可定义为

$$F_1 \approx \eta lv, \quad (2)$$

其中, η 为墨水的黏度, l 为银纳米线的长度, v 为涂膜速度^[31]。所制备的AgNWs的最小长度约20 μm ,墨水的黏度为1.59 mPa s,涂膜速度为60 mm/s,计算所得流体动力约1.91 nN,与文献[31,39]相比,大了两个数量级。随着流体动力的增大,有序化程度能进一步提升。我们通过预先在PET基底上旋涂一层PLL来减小摩擦阻力。同时,AgNWs上包覆的PVP聚合物与PLL层之间有范德瓦耳斯力,起着钉扎作用,从而增加AgNWs与基底之间的黏附力。通过增大毛细管作用力和流体动力,可大幅度增加银纳米线的有序化程度。

2.2 有序化程度的优化

本研究首先尝试了3种不同的清洗方法来调节AgNWs的纯化质量:(1)离心法。能成功保留AgNWs表面上PVP层(图2(a), (b)),所涂覆的TCFs上AgNWs密度较大,但银颗粒清洗得不干净,大幅度影响TCF的光学性能(图2(c))。(2)正压过滤法。如图2(d)~(f)所示,虽然银颗粒以及短棒清洗得很干净,但是由于AgNWs表面的PVP层也被清洗干净,大幅度减小了其与PLL之间的

图2 (网络版彩色)不同清洗方法下单根AgNW的TEM形貌图(a, b, d, e, g, h)及其有序化程度比较的OM照片(c, f, i)。(a)~(c)离心法;(d)~(f)正压过滤法;(g)~(i)动态搅拌法

Figure 2 (Color online) TEM images (a, b, d, e, g, h) of single AgNW with different purifying methods and OM images (c, f, i) of AgNW alignment degree comparison. (a)~(c) Centrifugation; (d)~(f) positive pressure filtration; (g)~(i) dynamic agitation method

扎钉作用力,导致TCFs上AgNWs密度大幅度下降。(3)动态搅拌清洗法。既成功保留了AgNWs表面上的PVP层(图2(g), (h)),又将墨水中银颗粒以及短棒清洗干净,制得的TCFs上AgNWs密度大,有序化程度高(图2(i))。将动态搅拌清洗的AgNWs分散在乙醇中时,涂覆得到的AgNW TCFs的有序化程度高于分散在水溶液及水和乙醇的混合溶液的纳米线(图S1(a)~(c))。因为用OSP-03涂膜棒刮涂后,首先得到的是湿膜,预有序化的AgNWs仍分散在溶剂里,倘若溶剂的蒸发速度过慢,或者干燥温度过高,都会造成AgNWs热运动过度,导致预有序化的AgNWs又重新变回杂乱无章的状态,从而影响最终TCFs上AgNWs的有序化程度。而且乙醇沸点较低,干燥速度快,无需加热烘干等操作,是最理想的溶剂。

前文指出OSP涂膜棒可以对AgNWs进行预有序化。当OSP涂膜棒上的凹槽宽度大于AgNWs长度时,会有大量杂乱无章的AgNWs直接通过涂膜棒,导致TCF上的AgNWs大部分都是随机取向分布的。如图S2(a), (b)所示,当用OSP-25涂膜棒(凹槽宽度为115 μm)和OSP-08涂膜棒(凹槽宽度为50 μm),涂覆得到的薄膜上的AgNWs都是随机取向分布。而用凹槽宽度为18 μm 的OSP-03涂膜棒所制备TCF上的AgNWs有序化程度很

高(图S2(c)). 因此, 涂膜棒的凹槽宽度对AgNW网络的有序化程度影响很大.

此外, 不同涂膜速度也会影响AgNW网络的有序化程度. 由图3(a)~(h)可以看出, 随着涂膜速度的降低, TCFs上的AgNWs的有序化程度先是逐渐增大; 当涂膜速度达到60 mm/s时, 有序化程度最佳, 之后又略有下降. 由于流体动力大小与涂膜速度成正比, 适当大小的流体动力能提高AgNWs的有序化程度, 但当流体动力的值大于AgNWs受到的摩擦阻力与PLL层之间的静电作用力之和时, AgNWs的附着力会大大减小, 导致TCFs上的AgNWs密度大幅度下降, 从而影响最终的有序化程度. 因此, 最佳的涂膜速度为60 mm/s.

另外, 不同浓度的AgNWs墨水所涂AgNW网络的有序化程度也不相同. 如图4(a)~(f)所示, 随着墨水中AgNWs浓度的增加, 所涂TCFs上的AgNWs密度也会增加. 而其有序化程度则先是随着AgNWs浓度的增加而增大, 当AgNWs浓度大于0.4 wt%时, AgNW网络的有序化程度趋向于稳定(图4(g), (h)). 由此可见, 增大AgNWs浓度, 并不能无限提高AgNW网络的有序化程

度, 墨水中最合适的AgNWs浓度为0.4 wt%.

2.3 AgNW TCFs的有序化表征

有序化程度参数 S_{2D} 可以通过以下公式获得:

$$S_{2D} = \langle 2\cos^2\theta_i - 1 \rangle, \quad (3)$$

其中, θ_i 为AgNWs排列的平均向量与第*i*根AgNW排列的向量之间的夹角^[54,55]. S_{2D} 在0~1之间, 越接近1代表AgNWs越对齐. $S_{2D}=1$ 时, 表示AgNWs完全按同一方向排列; $S_{2D}=0$ 时, 表示AgNWs完全随机取向.

在本研究中, 我们借助ImageJ软件来判断AgNWs的取向, 如表1所示, 由上述公式可以计算得出, 所制备的有序化AgNW TCFs的有序化程度 S_{2D} 最高可达0.82 (图5(a)~(h)), 表示有84%的AgNWs偏转角度在30°以内, 有81%的AgNWs偏转角度在15°以内, 远高于文献[41]的结果($S_{2D}=0.517$). 半峰宽FWHM仅为18.2°, 远低于文献[31,38,39]. 另外, 文献[40]中的其他计算公式:

$$S = \frac{1}{2}(3 \langle \cos^2\varphi \rangle - 1), \quad (4)$$

图3 (网络版彩色)不同涂膜速度下所制备的TCFs的OM照片(a~f), 有序化程度 S_{2D} 的变化(g)以及沿不同角度排布的银纳米线的数目分布图(h). (a) 50 mm/s, (b) 60 mm/s, (c) 90 mm/s, (d) 120 mm/s, (e) 150 mm/s, (f) 180 mm/s

Figure 3 (Color online) OM images (a~f) and alignment degree of TCFs prepared by different coating speeds (g) and count distribution of AgNWs arranged along different angles (h). (a) 50 mm/s, (b) 60 mm/s, (c) 90 mm/s, (d) 120 mm/s, (e) 150 mm/s, (f) 180 mm/s

图 4 (网络版彩色)不同浓度的AgNWs墨水所制备的TCFs的OM照片(a~f)、有序化程度 S_{2D} 的变化(g)以及沿不同角度排布的银纳米线的数目分布图(h). (a) 0.1 wt%; (b) 0.2 wt%; (c) 0.3 wt%; (d) 0.4 wt%; (e) 0.5 wt%; (f) 0.6 wt%
Figure 4 (Color online) OM images (a–f) and alignment degree (g) of TCFs prepared by AgNW inks with different concentrations and (h) count distribution of AgNWs arranged along different angles. (a) 0.1 wt%; (b) 0.2 wt%; (c) 0.3 wt%; (d) 0.4 wt%; (e) 0.5 wt%; (f) 0.6 wt%

表 1 制备的有序化AgNW TCFs的有序化程度与文献中报道的各种有序化TCFs的比较

Table 1 Comparison of the alignment degree of our aligned AgNW TCFs with reported various kinds of aligned TCFs in literatures

文献	涂布方法	表征方法	顺排程度	均匀性
[31]	棒涂	FWHM, FFT	FWHM = 21.4°(平面上)	√
[32]	喷涂	$S = \langle 2\cos^2\theta - 1 \rangle$	$S = 0.98$ (离喷嘴1 cm的平面上) $S = 0.87$ (离喷嘴1.5 cm的平面上)	×
[33]	喷涂	$S = \langle 2\cos^2\theta - 1 \rangle$	$S = 0.98$ (褶皱上) $S = 0.71$ (平面上)	×
[34]	喷涂	$S = \langle 2\cos^2\theta - 1 \rangle$	$S = 0.95, 0.93$ (平面中心) $S = 0.49, 0.27$ (平面边缘)	×
[38]	棒涂	FWHM	FWHM = 39.8°(小直径的通道内)	√
[39]	棒涂	FWHM, FFT	FWHM = 45°(平面上)	√
[40]	棒涂	$S_{ } = 1.5\langle \cos^2\theta \rangle - 0.5$	$S_{ } \approx 0.43$ (平面上)	√
[41]	棒涂	$S = \langle 2\cos^2\theta - 1 \rangle$	$S = 0.517$ (平面上)	√
本研究	棒涂	$S = \langle 2\cos^2\theta - 1 \rangle$	$S = 0.82$ (平面上)	√
	棒涂	FWHM, FFT	$S_{ } = 0.87$ (平面上)	√
	棒涂	$S_{ } = 1.5\langle \cos^2\theta \rangle - 0.5$	FWHM = 18.2°(平面上)	√

图5 有序化和交叉有序化的AgNW网络的OM照片(a, b)和沿不同角度排布的AgNWs的数目分布图(c, d). (a, c) 有序化AgNW网络; (b, d) 交叉有序化AgNW网络

Figure 5 OM images (a, b) and count distribution of AgNWs arranged along different angles (c, d). (a, c) Aligned AgNW networks; (b, d) across-aligned AgNW networks

其中, Φ 为AgNWs排列方向与初始方向之间的夹角. 通过式(4)以及ImageJ得到的数据, 本研究制备的有序化AgNW网络的有序化程度 $S=0.87$, 远远高于文献[40] ($S=0.43$).

然而, 有序化的AgNWs因其排列方向都基本相同, 导致AgNWs之间搭接的结点很少, 从而极大地影响了TCFs的导电性能. 因此, 沿着与第一次涂布方向呈 90° 的方向再次进行AgNW涂布, 最终得到交叉有序化的AgNW TCFs. 当其方阻在 $41.6 \Omega/\text{sq}$ 时, 其透过率可达 90.77% (含PET), 优于随机网络($T=89.47\%$, 图S3). 为了进一步扩大交叉有序化网络的AgNW TCFs在可拉伸电极中的应用价值, 我们用常规光刻法以及湿法刻蚀法对其进行图案化处理, 制备超细银纳米线导电通道, 观察其电阻的变化, 并与随机网络的进行比较, 以此来验证其结点的均匀性.

2.4 超细AgNW导电通道的制备

我们依次采用常规光刻法和湿法刻蚀法^[56]来制备超细AgNW导电通道(图S4), 最细的导电通道的宽度可达 $20 \mu\text{m}$. 在常规光刻法中, 通过调控前烘时间、紫外曝光剂量以及显影时间来制备超细光刻胶通道^[57]. 前烘是为了除去胶层中多余的溶剂, 防止其影响光刻胶

在显影液中的溶解度, 前烘过度则会影响光刻胶中感光剂的活性, 从而影响其在紫外光下的降解反应, 两者皆会影响最终图案的精度. 如图6(a)所示, 前烘时间为 60 s 时, 图案的精度基本都在 99% 以上, 延长或缩减前烘时间, 都会导致图案精度下降. 光刻胶AZ4620中含有叠氮醌类化合物, 在紫外光照射下, 会发生光解反应, 产生羧基, 大幅度提高水溶性, 最终可溶于碱性显影液中. 因此, 可用掩模版遮挡部分紫外光, 提高部分区域的水溶性, 利用不同区域之间的溶解度差异, 制备各种不同的图案. 由于光的反射与折射以及光解反应时光电子的传递等原因, 紫外曝光过度会造成图案的精度大幅度下降. 紫外曝光量不足, 则意味着光解反应不充分, 会导致光刻胶清除不干净, 最终影响AgNWs的刻蚀效果. 因此, 需要严格控制紫外曝光剂量, 最佳的曝光剂量为 $224 \text{ mJ}/\text{cm}^2$ (图6(b)). 光解反应后, 需要用强碱性的显影液去溶解曝光区域的光刻胶. 显影时间过长会造成光刻胶的残留, 从而影响AgNWs的刻蚀效果; 时间过长则会导致图案边缘(光电子传递区域)也被显影液溶解, 从而影响图案的精度. 尽管对于大宽度的通道来说, 边缘效应很微弱, 但对宽度小于 $100 \mu\text{m}$ 通道的精度影响却很大. 从图6(c)可以看出, 最佳显影时间为 5 s , 此时图案的精度都在 99% 以上. 制备的胶层通道可

图6 (网络版彩色)不同前烘时间(a)、紫外曝光剂量(b)以及显影时间(c)下AgNW导电通道精度的变化

Figure 6 (Color online) Changes of accuracies with AgNW conductive channels by different prebaking time (a), doses of UV radiation (b) and developing time (c)

以保护下面的AgNWs不被刻蚀, 经过NaClO浸泡后, 除了胶层下的AgNWs外, 其余地方的AgNWs全都被刻蚀成颗粒(图S5(a), (b)), 从而使未保护区域变得不导电。最后用无水乙醇清除多余的光刻胶。TCFs的光学性能会随着刻蚀时间的变化而变化, 如图S5(c), (d)所示, 最佳的刻蚀时间为10 s。此时TCF的透过率变化仅为0.04%, 雾度变化率仅仅为-0.12%。与其他的刻蚀剂相比, 用NaClO刻蚀后的TCF光学性能变化很小, 不会影响器件之后的使用。

2.5 超细AgNW导电通道的制备

取交叉有序化的AgNW TCFs, 沿着与AgNWs排布方向呈45°的方向, 用常规光刻法与湿法刻蚀制备超细AgNW导电通道, 如图7(a)所示, 在通道两旁涂上导电银浆, 干燥后测其电阻变化。图7(b~f)是分别用不同掩膜版制得的宽度为20~500 μm 导电通道的OM图。通过

测量其通道的宽度, 可以看出导电通道的精度均高于99%。交叉有序化的AgNW网络的结点分布比随机网络更规则, 在宽度减少到一定程度时, 结点数目会急剧减少。如图S6所示, 随机AgNW网络所制成的导电通道的两端电阻随着宽度的增大而增大, 其电阻与宽度的倒数呈一次函数的关系。而对于交叉有序化AgNW网络导电通道, 当其宽度缩短到50 μm 时, 其电阻比随机网络略有上升; 缩短到20 μm 时, 电阻急剧上升, 说明TCF沿着与AgNWs排布方向呈45°方向上的结点数目急剧减少, 证实了AgNWs的超高有序化程度以及其结点分布的有序性。

3 结论

利用改进的动态搅拌清洗法, 既可完美保留AgNWs表面的PVP层, 又可将原液中的有机物、银纳米颗粒和短棒清除干净, 保证AgNWs在TCFs上的密度

图7 (网络版彩色)导电通道的示意图(a)以及不同宽度下的光刻胶通道的OM照片(b~g)。(b) 20 μm , (c) 50 μm , (d) 100 μm , (e) 200 μm , (f) 300 μm , (g) 500 μm

Figure 7 (Color online) Schematic diagram of conductive channels (a) and OM images (b~g) of photoresist channels with different widths. (b) 20 μm , (c) 50 μm , (d) 100 μm , (e) 200 μm , (f) 300 μm , (g) 500 μm

以及有序化程度. 利用改进的Meyer棒涂法大幅度增大了促进AgNWs有序化的流体动力, 进一步提高了AgNW TCFs的有序化程度. 利用常规光刻法和湿法刻蚀对交叉有序化的AgNW TCFs进行简单图案化, 结果表明当导电通道宽度缩短至20 μm 时, 电阻急剧上升, 证实了TCFs上AgNWs的超高有序化程度以及其结点

分布的有序性, 为AgNW网络在可拉伸电极中的实际价值提供了理论依据. 同时, 银纳米线网络的有序化进一步提高了其导通概率与电导率, 在方阻达到器件要求的条件下, 进一步提高了其透过率, 为一些对光电性能要求较高的实际应用(例如触摸屏、显示器等)提供了一种新颖的优化路线.

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补充材料

图S1 不同溶剂的墨水所制备的TCFs的低倍SEM形貌图

图S2 不同型号的涂膜棒所制备的TCFs的低倍SEM形貌图

图S3 随机与有序化TCFs的低倍SEM形貌和透过率的变化

图S4 超细AgNW导电通道的制备流程

图S5 刻蚀前与刻蚀后的SEM形貌图以及其TCFs光学性能的变化

图S6 随机AgNW网络与有序化AgNW网络的导电通道两端的电阻与宽度的倒数的关系图

表S1 国际上制备有序化AgNW TCFs的方法及其优缺点

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Summary for “银纳米线网络的高有序排列及其图案化设计”

Highly ordered AgNW networks for patterning design

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Transparent conductive films (TCFs) are widely used in solar cells, displays, sensors, and energy storage systems. They should not only have excellent mechanical flexibility and optoelectronic properties, but also have feasibility in large area preparation while ensuring their uniformity and low cost. Indium tin oxide (ITO), a traditional TCF material, has some inherent shortcomings, such as high-vacuum deposition process, high deposition temperature, relatively high cost, and brittleness. Silver nanowires (AgNWs) based TCFs are the most promising candidate to replace ITO for their superior electrical and optical properties as well as excellent mechanical flexibility. So far, several methods have been used for preparing AgNW TCFs, such as blade coating, spray coating, spin coating, and vacuum filtration. However, a series of problems existed in these conventional processes, such as random distribution of AgNW networks, excessive junction resistance between AgNWs, and poor surface roughness. Therefore, a method for making aligned AgNW TCFs was proposed to solve the abovementioned problems. Researchers have produced aligned AgNW TCFs through various methods, such as capillary-assisted fluidic assembly, grazing incidence spraying, brush coating and electrohydrodynamic printing. All these methods show promising results, but to achieve a high degree of ordering and uniform distribution of AgNWs in large area is still a big challenge. In this paper, ultrathin AgNWs were prepared via a polyol reduction method, and AgNWs with a polyvinylpyrrolidone protective layer in inks were purified through an modified dynamic stirring cleaning method. Then, AgNW TCFs with a high degree of ordering were prepared on a polylysine pre-coated substrates through an improved bar coating method. Simple patterning was performed through the improved photolithography method and the wet etching method. The degree of ordering S_{2D} of the aligned AgNW TCFs obtained through this method was as high as 0.82, and the full width at half-maximum was only 18.2° . The ultra-high alignment degree of AgNW networks is ascribed to the substantial increase in the capillary force and hydrodynamic force. The minimum size obtained through patterning was as low as $20\ \mu\text{m}$, and the accuracy was as high as 99%. The change of TCF transmittance before and after the etching was only 0.04%, and the change of haze was only -0.12% . After simple patterning, the resistance rose sharply when the width of the conductive channels was reduced to $20\ \mu\text{m}$, confirming the ultra-high degree of ordering of the AgNWs on the TCFs and uniformity of junctions between the AgNWs. The strategy to fabricate highly ordered AgNW networks with tunable width of conductive channels provides a new route to practical applications of AgNW TCFs.

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