多层复合透明导电薄膜研究进展

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摘要 透明导电薄膜(TCF)兼具良好的导电性和透光性, 已作为电极被广泛应用于光电器件领域. 目前普遍使用的透明电极主要是铟锡氧化物(ITO)和掺铝氧化锌等透明导电氧化物(TCO)薄膜, 但由于ITO的生产需要稀缺原材料铟, 而其他TCO薄膜的导电性和可见光透明性尚需提高, 并且由于氧化物材料固有的脆性, TCO薄膜的柔性较差, 不能完全满足当前柔性电子器件的发展需求. 因而, 对于具有优异性能的无铟、柔性TCF的研究近年来受到研究者的广泛关注. 基于介质/金属/介质结构的多层复合TCF同时具有高的电导率、透光性以及良好的机械柔性, 可以满足目前柔性电子器件的应用需求, 而且其还具有功函数可通过选择介质层材料调节、可利用连续的卷对卷技术室温下在廉价塑料衬底上沉积等独特优势, 因而更具实用价值. 本文简要综述了近几年基于介质/金属/介质结构的多层复合TCF的研究工作, 首先分析了其透光率和面电阻对各层材料种类及厚度的依赖关系, 然后介绍了多层复合TCF的结构类型, 接着讨论了改善其综合光电性能的技术, 最后分析了其在光电器件领域应用时应考虑的其他重要性质.

关键词 透明导电薄膜, 介质/金属/介质, 多层复合, 超薄金属薄膜, 柔性

透明导电薄膜(TCF)同时具有良好的导电性和高透光性, 是许多光敏电子器件的重要组成部分, 在平板显示器、太阳电池、发光二极管、低辐射玻璃、防电磁干扰透明窗等领域具有广泛应用^[1,2]. 目前应用比较广泛的TCF主要是铟锡氧化物(ITO)和掺铝氧化锌(AZO)等透明导电氧化物(TCO)薄膜, 但由于ITO中包含昂贵的稀缺元素铟, 而其他TCO薄膜的导电性和可见光透明性尚需提高, 并且由于氧化物材料固有的脆性, 这些TCO薄膜的柔性通常较差, 已不能满足当前蓬勃发展的柔性电子器件的应用需求^[3,4].

近年来, 为克服传统TCO薄膜用作柔性透明电极时所固有的力学脆性和低温沉积时较差的导电性等限制, 基于石墨烯^[5]、碳纳米管^[6]、金属网格^[7]、金属纳

米线^[8]、超薄金属膜^[9]、纳米纤维^[10]、拓扑绝缘体^[11]等新兴纳米材料的TCF技术受到了人们的广泛关注. 在这些新型纳米结构TCF中, 银纳米线、金属纳米纤维和金属网格等金属纳米结构具有相对高的光透过率(550 nm波长光透过率可达90%)和低的面电阻(10~20 Ω/sq), 而在相同光透过率条件下, 基于石墨烯、碳纳米管和拓扑绝缘体的TCF的面电阻要比银纳米线薄膜大很多倍^[11,12]. 单纯的超薄金属膜虽可具有低的面电阻(4.5~8 Ω/sq), 但光透过率较低(75%左右)^[9], 因此基于金属纳米结构的TCF目前被认为是比较好的柔性透明电极候选材料. 然而, 单纯使用银纳米线、金属纳米纤维或金属网格作为透明电极的器件性能受其结构特点制约, 只提供整体电导率, 金属线之间是绝缘的,

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而且基于银纳米线和金属网格的透明电极都具有高的表面粗糙度,经常会造成器件短路故障.近年来,通过将这些金属纳米结构嵌入TCO或有机导电基质中形成复合电极,已可较好解决上述问题,并使电极的机械、热和化学稳定性得到增强^[9].此外,由于受限于当前印刷制作的工艺水平,金属网格透明电极常存在明显的莫瑞干涉波纹,而银纳米线和金属纳米纤维由于在导电薄膜中的不规则分布和其对光具有较强的散射作用,使得基于其的TCF常存在雾度问题.这种强的光散射效应,对基于银纳米线和金属纳米纤维的透明电极在太阳电池上的应用有时是有利的^[13],但对于其在显示器件上的应用则是不利的.

基于超薄金属薄膜的介质/金属/介质(DMD)结构多层复合薄膜是另外一种新型TCF,其导电性能主要取决于中间金属层,而两侧的介质层可有效抑制在可见光区来自金属薄膜的反射,从而使多层结构TCF在可见光波段具有良好的透光性.而且金属层材料所具有的良好导电性和延展性,使其甚至在介质膜被弯折破裂的情况下仍可具有良好的导电性,因此,与单层TCO薄膜相比,多层复合TCF具有明显更好的机械柔性.尽管与基于银纳米线的TCF相比其光透过率稍差,但二维形貌的银层不受银纳米线和金属网格几何特征所造成的上述技术问题的限制,而且银膜插于两层透明氧化物薄膜之间的构型,也有利于防止银氧化进而保证银层电学性质的长期稳定.此外,多层复合结构TCF在制备过程中不需要加热,在室温条件下就可以制备出具有良好光电性能的薄膜,因此更加便于利用卷对卷技术在廉价塑料衬底上实现大面积低成本制备.多层复合结构TCF的功函数还可以通过选择不同介质层材料来调节,从而可以更好地满足不同电子器件的个性化需求.多层复合结构TCF具有的上述优点,使其作为透明电极在柔性电子器件领域具有巨大的应用潜力^[14].

本文综述了近几年基于DMD结构的多层复合TCF的研究工作,首先分析了其透光率和面电阻对各层材料种类及厚度的依赖关系,然后介绍了多层复合TCF的结构类型,接着讨论了改善其综合光电性能的方法和技术,最后分析了多层复合TCF在光电器件领域应用时应考虑的其他重要性质.

1 多层复合TCF中各层材料和厚度选择

DMD结构多层复合透明电极主要利用中间薄金

属层来获得良好的导电性,并利用两侧介质层来提升电极整体透明性.图1给出了DMD多层结构电学行为示意图.多层电极的整体表面电阻为 R_s ,电路图中的电阻分别代表介质层(R_D)及金属层(R_M),其中 $1/R_s=1/R_M+2/R_D$.由于通常金属的电阻率远小于介质,例如,考虑 $R_D=100R_M$,则 $R_s=R_M/1.02\approx R_M$.因此,多层电极的整体表面电阻主要由金属层决定.由于多层结构中光的干涉和金属/介质界面处的表面等离子激元(SP)效应,金属层两侧介质层材料的折射率和膜厚对多层电极整体透过率有重要影响.通过合理选择介质层材料和厚度,利用光在多层膜中的相消干涉及高折射率介质层材料对SP激发的有效抑制,可大幅改善多层电极整体的光学透明性^[15].

TCF的表面电阻(R_s)和光透过率(T)是衡量其光电性能的两个基本参数,均与薄膜厚度密切相关.薄膜厚度越大, R_s 越小, T 也越小,因此薄膜的透光性和导电性通常是矛盾的.为了评价不同TCF的综合光电性能,Fraser和Cook^[16]定义了品质因子 $F=T/R_s$.然而,在应用时人们注意到该定义中 R_s 所占权重过大,使得薄膜最大的 F 值只在相对较大的膜厚和低 T 的情况下才能获得.为此,Haacke^[17]提出用 T^{10}/R_s 来定义 F ,从而更加突出光学透明的重要性.然而,由于所测 T 上的差异,比较不同研究给出的 F 值有时是比较困难的.文献中,透明电极的 T 有时指在某一具体波长 λ 处的透过率,其中 λ 为550 nm(人眼对该波长的光灵敏度最高)和 T 的最大值对应的波长两种情况最为常见,但有时在某一光波段内($\lambda_1\sim\lambda_2$)的平均值也经常被使用.此外,有时 T 仅指涂层(测量时相对于基材),但有时 T 也包括基材的光吸收(测量时相对于空气),可以使 T 值降低约10%.表1列出了最近几年多

图1 (网络版彩色)DMD多层结构电学行为示意图

Figure 1 (Color online) Schematic representation of the electrical behavior of DMD multilayer structures

表1 近几年多层复合TCF相关研究的一些典型实验结果

Table 1 Summary of some typical experimental results on multilayer composite TCF in recent years

多层膜结构	最佳厚度 (nm)	衬底	T(%)	波长范围 (nm)	R_s (Ω/sq)	器件应用	电极 类型	文献
铜锌氧化物(IZO)/Ag/IZO	30/10/30	玻璃	86.9	550	3.6	OLED	阳极	[18]
铜铟锡氧化物(IGZO)/Ag/IGZO	39/19/39	PET	88.8	500	5.09			[19]
锰掺杂氧化锡(MTO)/Ag/MTO	40/11/40	玻璃	85.4	380~780	10.6	OSC	阳极	[20]
掺氟二氧化锡(FTO)/Ag/FTO	20/7/30	石英	95.5	380~780	8.1			[21]
CuAlO ₂ /Ag/CuAlO ₂	40/8/40	玻璃	89.2	550	9.6			[22]
ZnS/Ag/WO ₃	40/20/5	PET	60	550	6	OLED	阳极	[23]
TiO ₂ /Ag/ITO	30/8/45	玻璃	88	375~700	6.2	OPV	阴极	[24]
TiO _x /Ag/WO ₃	40/15/40	PES	93.5	550	3.97			[25]
TiO ₂ /Ag/AZO	30/8/40	玻璃	87.7	375~700	6.3	OPV	阴极	[26]
WO ₃ /Ag/MoO ₃	共100 nm	玻璃	81.7	550	9.75	OLED	阳极	[27]
ZnO/Au/ZnO	30/8/30	玻璃	86.2	650	14.31			[28]
PEDOT:PSS/Au//PEDOT:PSS	35/15/35	PET	82.6	485	20.9			[29]
SnO _x /Au/SnO _x	35/5/35	石英	83	475~800	52			[30]
ZnO/Cu/ZnO	40/10/40	玻璃	85	500~750	12	OPV	阳极	[31]
MoO ₃ /Al/MoO ₃	30/15/5	PES	70	550	7	OLED	阳极	[32]
AZO/Pd/AZO	50/7/50	玻璃	83.2	550	45			[33]
AZO/Mo/AZO	30/15/30	玻璃	75	380~780	13.31			[34]
ITO/Ni/ITO	50/5/45	聚碳酸酯(PC)	76	550	32			[35]
ZnO/In/ZnO	50/8/50	玻璃	72	550	1600			[36]
AZO/CrCu/AZO	54/8/54	玻璃	85	300~1100	99			[37]
ZnS/Cu/Ag/ZnS	50/3/9/45	玻璃	85	400~1000	4.8			[38]
MoO ₃ /Au/Ag/MoO ₃	2/1/7/5/50	玻璃	88.7	500~2000	16	钙钛矿电池	阴极	[39]
MoO ₃ /Au/Ag/MoO ₃	3/1/7/5/50	玻璃	83	580	19	OPV	阳极	[40]
ZnS/Ag/ZnO/Ag/WO ₃	35/12/100/20/45	PET	82	550	2.17	OLED	阳极	[41]
ZnS/Ag/ZnS/Ag/ZnS	30/12/30/12/30	玻璃	75.5	550	2.7	OLED	阳极	[42]
ZnO/AgO _x /ZnO	50/8/50	PET	91	400~1000	20	OPV	阴极	[43]
ITO/AgO _x /ITO	30/8/30	PET	88	600	20	OPV	阴极	[44]
ZnO/AgO _x /ZnO	40/10/40	PET	95.9	570	8.11			[45]
ZnO/CuO _x /ZnO	60/8/60	PET	83.2	400~800	9.0	OPV	阴极	[46]

层复合TCF领域的一些典型研究结果, 当同一文献中对不同金属或介质层厚度样品进行了表征时, 表1中只列入了被作者选作最佳性能的结构. 对于更早期的一些研究结果, 可参见文献[14].

1.1 金属层材料和厚度选择

为使多层复合TCF具有更好的导电性和透明性, 通常应尽量选择电阻率更低、在目标应用所关注的光波段内光吸收系数更小的金属. 目前在多层复合TCF研究中, 已被用作中间金属层的材料主要有

Ag^[18~21,24,25,47], Au^[28~30], Cu^[31,48], Al^[32,49], Pd^[33], Pt^[50], Mo^[34], Ni^[35], In^[36]以及一些金属合金^[37,51]等, 其中用Ag, Au和Cu作为金属层的报道较多, 而其他金属材料仅有很少的文献报道.

由于Ag具有最好的导电性和在可见光波段小的光吸收系数, 因此应用最为广泛. 从表1可以看到, 利用Ag作为中间金属层, 并利用ITO, AZO等多种材料作为介质层均可获得光电性能优良的多层复合TCF. 这表明一个足够薄且连续的金属膜在可见光波段可以是透明的, 并同时具有良好的导电性. 然

而,需要指出的是,当金属膜的厚度低于某一临界膜厚时,其电阻率和光吸收则迅速增加^[52,53].为了展示多层复合TCF的光透射率和表面电阻随金属层厚度的常见变化规律,图2给出了利用磁控溅射技术改变Ag层厚度在玻璃衬底上制备的ITO(40 nm)/Ag/ITO(40 nm)多层结构薄膜平均光透过率(400~800 nm)和表面电阻对Ag层厚度的依赖关系.从图中可以看出,随着Ag膜厚度的增加,样品的平均光透过率呈现了先增加后减小的趋势,并在Ag膜厚度为9 nm时达到最大,而样品的表面电阻则呈现了先陡然下降,在7 nm后逐渐趋于平缓的趋势.多层复合TCF的这种演变与金属薄膜生长过程中从金属团簇向连续膜层的过渡紧密相关.一般情况下,这种过渡的临界厚度取决于金属种类、所用基材和沉积条件^[54,55].通常金属均以岛状模式在衬底上生长,在薄膜生长初期并不能直接形成连续膜,而是先处于由分散的岛状金属颗粒组成的状态,此时薄膜的表面电阻会很大.由于金属颗粒的局域SP效应^[56,57],其对光有很强的吸收和散射作用,使薄膜的光透过率也会较低.当金属膜的纳米结构消失而形成连续薄膜时,局域SP效应消失,薄膜的光透过率会明显改善,而表面电阻更会陡然减小.之后,随着金属膜层厚度的进一步增加,薄膜的光透过率会不断降低,而表面电阻会缓慢降低,但其通常仍大于相应体金属材料的电阻率值.

与Ag相比,Au具有更优秀的耐腐蚀性,而Cu的成本更低,因此基于Au和Cu作为中间金属层的多层复合TCF近年来也多有报道.利用Cu或Au作为中间

金属层,也已实现了方阻低于10 Ω/sq 的多层复合TCF的制备^[28~31,48],但其最大透过率一般出现在550~600 nm附近,与使用Ag作为中间层的TCF相比,其在500 nm波长附近的光透过率明显更低.这是由于Cu和Au具有比Ag更小的等离子体频率,使其在可见光的短波长区域具有更强的光吸收^[58,59].当Cu和Au层的厚度增加时,与Ag层的情况相比,其随厚度增加薄膜光透过率减小的速度更快,为了保持与Ag膜情况同样高的光透过率值,就需要更低的膜厚上限.这一点对于其他金属更为重要,例如,当Ni厚度大于10 nm^[52]或Pt厚度大于6 nm^[50]时,多层膜的透过率最大值低于60%,而厚度太薄,则通常不足以获得适合应用的低的表面电阻值.利用Al作为中间金属层的ZnO/Al/ZnO结构也已被报道,但是其光学和电学特性仅在300 $^{\circ}\text{C}$ 以上退火后才有所改善,可以达到典型AZO单层电极的值^[49].最近,Zhang等人^[33]报道了AZO/Pd/AZO多层复合TCF,但其电学特性仅在400 $^{\circ}\text{C}$ 的氢气氛下退火后才有所改善.

此外,利用合金作为中间金属层也有少量报道^[34~38,51,60,61].对几种Ag基金光电特性的测量结果显示,少量Cu或Au的掺入(约5%~10%,质量百分比)对Ag膜的透过率和面电阻影响很小,但对于Pd元素,为了避免表面电阻的显著增加,其掺入量应小于2%(质量百分比)^[60].利用AgPd合金制备的AZO/AgPd/AZO结构的多层TCF的最佳光透过率可达90%,最低电阻率为 $8.28 \times 10^{-4} \Omega \text{ cm}^{[61]}$.Mouchaal等人^[38]研究了ZnS/Cu/Ag/ZnS结构多层复合TCF,通过利用双层金属Cu/Ag作为中间层使多层膜的高透光率光谱范围明显加宽,其在400~1000 nm波段的平均光透过率可达85%,表面电阻也仅为5.0 Ω/sq .

1.2 介质层材料和厚度选择

多层结构中金属/介质界面处的SP耦合和光的干涉效应,对多层电极整体透过率有重要影响.SP耦合是由金属中导电电子激发所诱导的电子的集体振荡,其通常在金属与介质材料的界面处产生^[62].由于平面SP耦合的非辐射特性,这种电子的集体振荡能量将以非辐射形式耗散,造成入射光能量损失,使光透过率降低^[15].通过使用比相应金属具有更大介电常数的介质层,可以抑制介质/金属界面的SP耦合的发生,因此,使用更大介电常数的介质材料通常可增加多层膜的光透过率^[63].

图2 (网络版彩色)ITO(40 nm)/Ag/ITO(40 nm)多层膜平均光透过率(400~800 nm)和表面电阻作为Ag层厚度函数

Figure 2 (Color online) Average transmittance (400~800 nm) and sheet resistance of the ITO(40 nm)/Ag/ITO(40 nm) multilayer films as the function of Ag layer thickness

除介电常数外, 介质层厚度对多层膜的光透过率也有重要影响. 通过选择合适的介质层厚度, 利用光在多层膜中的相消干涉, 可以显著增加光透过率. 为展示DMD结构光学性质对介质层厚度的典型依赖关系, 图3(a)给出了采用光学模拟软件改变ITO层厚度计算得到的ITO/Ag(10 nm)/ITO结构的透射和反射光谱, 图3(b)为该多层结构在400~800 nm波段的平均光透过率作为ITO层厚度的函数. 考虑到通常在10 nm厚度Ag已经可以形成连续薄膜, 因此在计算中假定各膜层均是平的, 同时假定Ag和ITO薄膜的光学介电常数均不依赖于层厚. 从图中可以看出, 随ITO层厚度的增加, 平均光透过率先升高后降低, 而平均光反射率先降低后升高. ITO层厚度为40 nm时, 平均光透过率达到最大值(88.4%), 此时平均光反射率最

小, 与ITO层厚度为0 nm的纯Ag薄膜相比, 其平均光透过率增加了将近20%. 这表明金属层两侧的适当厚度ITO层能够有效降低来自金属表面的光反射, 并提高整个结构在可见光区的透过率. 应该指出的是, 由此产生的曲线的确切形状也取决于ITO层的厚度(图3(a)), 随ITO层厚度的增加, 光透过率最大值所对应的波长向长波方向移动. 因此, 可以通过改变介质层厚度来调整这些特性, 使其满足光电器件对电极的具体应用需求.

需要指出的是, DMD多层结构的横向导电性主要由金属层控制, 不依赖于介质层的性能. 利用DMD多层电极收集或注入载流子的过程中, 由于载流子的横向输运主要发生在金属层, 只有垂直输运发生在介质层内部, 因而介质层的导电性能主要影响载流子在器件中的垂直输运. 例如, 对于太阳能电池, 多层结构中介质层的导电性能会影响器件整体的串阻, 介质层导电性差会导致器件的短路电流减小和填充因子降低^[64]. 因此, 多层复合TCF在电子器件领域实际应用时也应适当考虑介质层的导电性能.

2 多层复合TCF的结构类型

DMD结构多层复合TCF中, 介质层材料可以是TCO, 也可以是电介质. 对于DMD多层结构薄膜的研究, 可追溯到20世纪50年代, Holland和Siddall^[65]发现在Au薄膜两侧制备Bi₂O₃薄层, 可以使Au薄膜的光透过率明显增加. 1974年, John等人^[66]研究指出DMD结构多层薄膜能够抑制从金属层反射的光波, 从而获得波长可调的高光学透过率. 但在20世纪70, 80年代, DMD多层结构薄膜主要被用作低辐射薄膜, 而其作为透明电极在当时很少有报道, 直到近些年才得到人们的关注. DMD多层结构薄膜用作透明电极, 最早始于1998年Bender等人^[47]的工作, 他们最初的目的是提高ITO薄膜的导电性. 实际上, 对于小面积器件, 利用ITO层作为电极是非常成功的, 但是其应用在大面积光电器件上时, 由于ITO导电性的限制引起了串联电阻出现, 从而降低了器件性能. 为增加ITO的导电性, 他们提出了在ITO薄膜中插入金属层的想法, 利用ITO/金属/ITO多层结构来替代单层ITO, 并获得了令人满意的导电性能, 同时大幅减少了ITO层厚度, 使电极制作成本也得到降低. 之后, 人们使用其他TCO材料实现了无钢结构. 为了调整电极功函数或利用高折射率的介质材料来改善多层

图3 (网络版彩色)(a) 采用光学模拟软件计算所得的不同ITO层厚度条件下ITO/Ag(10 nm)/ITO的光学透射和反射光谱. (b) ITO/Ag(10 nm)/ITO在400~800 nm波长范围内的平均光透过率和反射率作为ITO层厚度的函数

Figure 3 (Color online) (a) Optical transmittance and reflectance spectra for ITO/Ag(10nm)/ITO with different ITO layer thickness calculated by optical simulation software. (b) Average transmittance and reflectance of ITO/Ag(10 nm)/ITO at the wavelength range of 400~800 nm as the function of ITO layer thickness

膜的光透过率等,人们研究了非TCO材料作为介质层的多层复合透明电极. Liu等人^[67]提出采用ZnS/Ag/ZnS多层复合TCF作为平面显示器透明电极的可行性. Sahu等人^[68]利用电子束蒸发法制备了AZO/Ag/AZO无铟多层复合TCF,所得最佳薄膜的方阻为7.7 Ω/sq ,可见光透过率为85%.与仅使用TCO作为电极相比,DMD电极的金属层提供了高的横向导电性,因此介质层通常不必具有高导电性.例如,Hong等人^[69]用热蒸发法在室温下制备了 $\text{WO}_3(30\text{ nm})/\text{Ag}(12\text{ nm})/\text{WO}_3(30\text{ nm})$ 多层复合TCF,展现了优异性能,其方阻仅为8.4 Ω/sq ,510 nm波长的光透射率可达93.5%.尽管热沉积的 WO_3 薄膜的本征电导率比ITO,AZO等TCO薄膜低几个数量级^[70],但 $\text{WO}_3/\text{Ag}/\text{WO}_3$ 的表面电阻与最好的ITO/Ag/ITO或AZO/Ag/AZO电极的表面电阻却是相当的.DMD结构的这一特点,使人们可以在更广的范围选择介质层材料.近年来,多个研究组陆续开展了DMD结构多层复合TCF的研究,目前常用作介质层的电介质材料有 ZnO ^[28,48], TiO_2 ^[24], ZnS ^[38], WO_3 ^[25]和 MoO_3 ^[32]等,TCO材料有ITO^[18,35,60],AZO^[28,33,34,51],IZO^[18],IGZO^[19],MTO^[20],FTO^[21],掺镓氧化锌(GZO)^[50]等,这些TCO一般都是n型的;但一些p型材料也可以使用,比如 CuAlO_2 ^[22].此外,有机透明导电材料(PEDOT:PSS^[29]等)也已被用作DMD结构的介质层.

除了上述对称结构外,DMD结构还可以是非对称的,即金属层两侧的介质层材料可以是不同材料.通过选择不同电介质或TCO材料来调节功函数和光学折射率,从而可以更好地满足不同电子器件的个性化需求.2009年,Cho等人^[23]用热蒸发技术在聚对苯二甲酸乙二醇酯(PET)基材上制备了具有非对称结构的ZnS/Ag/ WO_3 多层复合透明电极,具有高功函数特征的 WO_3 提升了器件的空穴注入能力,具有高折射率的ZnS(550 nm波长时,折射率 $n=2.35\pm0.05$)提高了多层电极的光透过率.基于该电极所制备的有机发光二极管(OLED)器件的开关电压为2.4 V,在1000 cd/m^2 条件下发光效率为6.2 cd/A ,外量子效率最大值为2.0%,同时具有较好的耐弯曲特性,性能明显优于相应的ITO基OLED器件. Formica等人^[26]在柔性玻璃衬底上利用磁控溅射技术沉积了 $\text{TiO}_2/\text{Ag}/\text{AZO}$ 结构透明电极,通过优化各膜层厚度,其所得最佳薄膜的方阻为6.3 Ω/sq ,在350~700 nm波段平均光透过率为87.7%,制备的有机太阳电池(OPV)的转换效率为

6.6%,是ITO作为电极所制备相应电池效率的85%以上,且具有良好的柔性,最大与最小半径(6和3 cm)下弯折400次后,电池效率仍可达到初始值的94%.

三层结构TCF展示出与ITO可比的表面电阻和可见光透过率,可以满足许多光电器件的应用需求,但大面积OPV、大面积显示等器件通常需要透明电极具有更低的表面电阻.通过增加金属层厚度降低三层结构TCF的表面电阻时,界面处反射光束与通过多层结构和透明基材的相应透射光束之间的干涉不能完全相消,不能很好地抑制来自金属薄膜的反射,因此基于厚金属层的多层结构TCF的可见光透过率很低.为了解决上述问题,近年来多于三层的介质/金属复合结构TCF也有少量报道^[41,42]. Lee等人^[41]在PET衬底上制备了 $\text{ZnO}/\text{Ag}/\text{ZnO}/\text{Ag}/\text{WO}_3$ 结构透明电极,通过在两层Ag之间引入ZnO夹层,使该多层膜具有极低的表面电阻(1.6 Ω/sq),优化各膜层厚度所得的样品具有高且宽的透过率谱峰(平均光透过率为75%). Yang等人^[42]在PET衬底上制备了 $\text{ZnS}/\text{Ag}/\text{ZnO}/\text{Ag}/\text{WO}_3$ 结构TCF,在表面电阻为2.17 Ω/sq 时仍具有超过80%的光透过率.

3 改善多层复合TCF光电性能的技术进展

表面平滑超薄连续金属薄膜的沉积对于获得高性能的多层复合TCF至关重要.目前,利用真空沉积技术制备超薄连续光滑金属薄膜的主要挑战,来自于金属薄膜沉积初期的岛状生长效应.为了实现高透明,金属层薄膜应尽可能薄.然而,在金属薄膜沉积初期,金属粒子趋于在基板上形成孤立的岛,这种不形成连续、平坦的小颗粒层而是岛状生长的趋势,极大地限制了金属薄膜在小厚度情况下的导电性.为了使金属膜导电,就必须达到一个临界厚度(渗流阈值厚度),反过来又限制了薄膜的透明度.此外,粗糙的金属表面和孤立团簇在可见光波段会引起局域SP共振吸收,将大大降低薄膜的透光性.因此,为同时提升多层复合TCF的光透过率和电导率,需要降低金属膜沉积时的渗流阈值厚度.一般情况下,渗流阈值厚度取决于衬底、沉积条件及金属的种类^[57,58].控制金属在衬底或下面介质层上的润湿性是减少表面粗糙度、使渗流阈值厚度降低,进而减小整个多层复合薄膜电阻并增加其透明性的关键.

近年来,为获得综合性能更加优良的多层复合TCF,人们运用多种技术来调控金属对生长表面的

润湿性,以降低金属层的渗流阈值厚度,比如,在Ag膜沉积前引入高能籽晶层^[40,71,72]、在银膜沉积时引入合适的掺杂剂^[43,44,46,73,74]或者控制薄膜沉积速率^[73]等. Formica等人^[72]用Cu作为籽晶层制备了稳定的原子级平滑的超薄Ag膜. 通过引入最小0.5 nm的Cu籽晶层,沉积Ag膜的渗流阈值厚度可降低3~4 nm,表面均方根粗糙度降至0.5 nm以下(图4),并且具有很好的稳定性,在大气环境下存放4个月后电学性能几乎保持不变. Zhang等人^[73]用共溅射薄膜沉积技术在Ag膜中掺杂微量Al,制备了超薄、平滑和低损耗的Al掺杂Ag膜. 少量Al的引入可有效抑制薄膜生长初期Ag岛的形成,更利于连续Ag膜的生长. 最近, Wang研究组^[43,44]通过在Ag层沉积时引入微量氧制备的ITO/Ag/ITO和ZnO/Ag/ZnO薄膜,在导电性基本没有降低的情况下,其光透过率得到了大幅提高. Zhao等人^[46]报道了在Cu膜沉积时微量氧(5%左右)的引入可显著改善Cu在ZnO薄膜表面的润湿性,使Cu膜的渗流阈值厚度明显降低,基于此制备的ZnO/CuO_x/ZnO多层TCF表现出了良好的光电性能,在400~800

nm可见光波段的平均光透过率为83%,表面电阻为9 Ω/sq. Nguyen等人^[75]研究了沉积速率对MoO₃/Ag/MoO₃多层复合TCF的光电特性的影响,结果发现Ag膜的渗流阈值厚度依赖于热蒸发制备Ag薄膜时的沉积速率,通过控制金属薄膜的沉积速率可在一定程度上改变其渗流阈值厚度.

4 多层复合TCF的其他特性

除了光电特性外,在实际应用中多层复合TCF的功函数、工艺兼容性、机械柔性及稳定性等问题也须考虑. 在光电器件中,透明电极和相邻层之间的能带结构对器件性能起着至关重要的作用. 例如,当透明电极被用作有机光电器件的阳极时,对于OPV或OLED器件,与阳极接触的有机材料通常则分别是电子施主层或空穴传输层,如果透明电极的功函数与有机材料最高占有分子轨道之间有较强的能级差,接触后会在TCF/有机材料界面处形成势垒,该势垒将降低OLED的空穴注入效率. 而对于OPV来说则将降低空穴收集的效率,因此,必须改善透明电极与有机层之间的能带匹配. 通常DMD电极的功函数主要由上部的介质层决定^[76],例如,ITO/Ag/ITO, ITO/Ni/ITO样品展示了与类似的单层ITO电极相同的功函数^[52,76,77],而Ni掺杂的ITO则具有比纯ITO薄膜更高的功函数^[78].

通过选择不同的介质层材料可以调整DMD电极功函数,而且DMD结构的表面电阻仅轻微依赖于介质层材料的电阻,使介质层材料的选择具有很大的灵活性. 与其他形式的透明电极相比,DMD结构多层电极在满足不同光电器件对功函数的个性化需求方面具有独特优势. 近年来,人们已将多层复合TCF用作多种光电器件的阳极、阴极和中间电极^[27,79,80]. 例如, Zadsar等人^[27]用WO₃/Ag/MoO₃作为阳极制备OLED,器件结构为阳极/PEDOT:PSS/TPD/Alq₃/LiF/Al. 与ITO为阳极的相同结构器件相比,其最大功率效率(0.31 lm/W)和电流效率(1.2 cd/A)分别提升了58%和41%. Ghosh等人^[24]用TiO₂/Ag/ITO作为glass/TiO₂/Ag/ITO/sol-gel ZnO/PTB7:PC₇₁BM/MoO₃/Ag结构倒置OPV的阴极,制得的电池光电转化效率为8.34%,优于ITO基的相应电池转换效率(8.15%). Lee等人^[80]用MoO_x/Ag/MoO_x多层膜作为叠层OPV的中间电极,制备的聚合物/小分子叠层OPV的转换效率达到5.6%,高于相应的单结电池,短路电流密度为

图4 (网络版彩色)(a) 6 nm Ag和(b) 1 nm Cu/6 nm Ag的二维原子力显微镜(AFM)图; (c) 有无Cu籽晶层的Ag膜电阻率变化比较. 图中虚线表示利用相同溅射过程沉积的300 nm厚Ag膜的电阻率^[23]

Figure 4 (Color online) Two-dimensional AFM images of 6 nm Ag (a), 1 nm Cu/6 nm Ag (b). (c) Comparison of electrical resistivity variation for Ag films with and without a Cu seed layer. The dashed line represents the resistivity of bulk Ag film of about 300 nm thickness deposited using the same sputtering process^[23]

12.8 mA/cm². 许多实验结果表明, 更加匹配的功函数和更低的面电阻使多层电极用于OLED时, 可以减小驱动电压和器件中热的产生; 而用于OPV器件时可以提高其填充因子和电流密度. 另外, 考虑到多层电极在可见光波段的选择性透明特性, 其高透光率光谱范围与器件光敏层的发射(或吸收)波段的匹配程度, 也是影响器件效率的重要因素.

从制备工艺与器件的兼容性角度考虑, 制备多层复合TCF时一般衬底是不需要加温的, 这样制备出的多层膜中的介质层大部分情况下是非晶态的, 但由于DMD多层膜的导电性主要依赖于金属层, 因此介质层是否为晶态对多层膜整体的导电性能影响不大. 多层复合TCF的一个显著的优点是在低温下制备, 使其适合于在不能耐受高温的廉价塑料衬底上沉积, 也与OPV, OLED等有机光电器件的低温制备工艺兼容. 在不加热的塑料基板上利用卷对卷技术连续地进行透明电极的沉积, 在处理成本、处理速度和热预算方面均具有无可比拟的优势. 然而, 这需要所沉积的电极薄膜具有良好的机械柔性, 能够很好地耐受制备过程中薄膜的伸直和弯曲. 由于金属层的良好导电性和延展性, 使其即使在介质层被弯折破裂的情况下, DMD结构整体仍可具有良好的导电性, 因此多层复合TCF比单层TCO具有更好的机械柔性, 并已被弯曲测试实验证实. Park等人^[81]利用卷绕式溅射薄膜沉积系统在PET基材上制备了ITO/Ag/ITO多层膜, 其方阻为4.28 Ω/sq, 光透过率为89.28%, 并具有良好的机械柔性. 弯曲测试结果如图5所示, 其表面电阻的相对变化率在4000次弯折中始终为常数, 值得注意的是, 弯曲ITO/Ag/ITO电极会使其电阻增加, 伸展后其电阻又恢复到初始值. Ou等人^[39]用DMD多层膜和超薄Au膜分别作为顶和底电极制备了柔性半透明钙钛矿太阳电池, 其整体转换效率为8.67%, 在500~2000 nm的平均光透过率为15.94%. 通过减小Au底电极的厚度, 平均光透过率可进一步增加至31.61%. 该电池展示了良好的柔性和机械强度, 在3.9 mm的弯曲半径下弯折1000次后, 电池效率仍保持初始时的88%.

DMD电极的稳定性对器件的应用也非常重要. 由于多层复合TCF通常制备温度较低, 其层与层之间以及膜与基底之间的应力状态和热膨胀系数不同, 使其与高温制备的TCO薄膜相比, 环境稳定性稍差. 为提高薄膜的稳定性, 蒸镀一层阻隔层或者在金属

图5 (网络版彩色)(a) 由斜Cu夹夹着的ITO/Ag/ITO电极的初始位置 and 弯曲位置图. (b) 反复弯曲后利用卷对卷沉积的ITO/PES和ITO/Ag/ITO/PES样品的归一化电阻作为弯折次数的函数. 插图显示了柔性非晶ITO和ITO/Ag/ITO电极的电阻随弯曲次数的变化^[77]

Figure 5 (Color online) (a) Picture of the initial position and flexed position of the ITO/Ag/ITO electrode clamped by the tilted Cu clamp. (b) Normalized resistance change after repeated bending as a function of the number of cycles for roll-to-roll sputtered single ITO/PES and ITO/Ag/ITO/PES samples. The inset shows the variation of the resistance of the flexible amorphous ITO and ITO/Ag/ITO electrodes with the number of bending cycles^[77]

中掺杂其他合适的元素等都是有效的方法. 在Ag膜上镀一层很薄的Ti, Ti层在高温下可以生成氧化物来保护Ag层, 进而增加了Ag膜的热稳定性^[82]. 在Ag膜中掺杂Al可以改善薄膜的热稳定性^[74,83], Ag中掺入Pd可以提高薄膜的耐湿性, 在Ag中同时掺入Pd和Cu, 能够防止中间金属层的聚集和氧化, 使该多层膜在大气条件下更加稳定^[51,60,61]. 最近, Zhang等人^[45]在Ag膜沉积时掺入微量氧, 制备的ZnO/Ag/ZnO结构多层TCF, 显示了良好的稳定性, 暴露于大气放置6个月光电性能仍十分良好.

5 结论与展望

由于ITO中铟元素的稀缺性和包括ITO在内的传统TCO薄膜的柔性差, 无铟柔性透明电极已成为近年来TCF领域的研究热点. DMD结构多层复合TCF主要利用中间薄金属层来获得良好的导电性, 金属层的高电导率允许金属层足够薄, 因此能够在具有良好导电性的同时也拥有较好的透光率, 而两侧的介

质层可以抑制在可见光波段来自金属层的反射,进而提供更高的选择性透明.大量实验已表明,基于多种TCO(或电介质)与金属组合的多层复合TCF,可以获得比单层TCO更好的光透过率和表面电阻值,通过选择不同介质层材料可以实现对其功函数的调整,能更好地满足不同电子器件对透明电极功函数的个性化需求,已被广泛用于光电器件的阳极、阴极甚至中间电极.此外,DMD结构多层膜具有良好的机械柔性,而且各层薄膜均可利用真空沉积技术在不加热条件下制备,使其非常适合在不耐高温的塑料基板上利用卷对卷技术进行连续沉积,在处理成本、处理速度和热预算方面都是传统TCO生产无法比拟的.

由于金属薄膜生长初期的岛状生长特性,通常存在最佳金属层厚度使多层复合TCF的品质因子最大,降低金属薄膜的渗流阈值厚度可有效提升多层复合TCF的综合光电性能.尽管DMD结构多层复合TCF在多方面的性能已经十分优异,但进一步提升其透明性和导电性,尤其是拓展其高透过率光谱范围,对其在太阳电池等需要宽光谱透过率电极的器件中的应用仍十分必要.此外,多层复合TCF长期环境稳定性问题也需要更广泛和深入的研究.可以预期,在该领域研究者的不断努力下,多层复合TCF必将在新一代柔性透明导电薄膜的竞争占据一席之地.

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Summary for “多层复合透明导电薄膜研究进展”

Recent progress of multilayer composite transparent conductive film

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Transparent conductive films (TCFs), which transmit light and conduct electrical current simultaneously, are widely used as transparent electrodes across technical fields such as flat-panel displays, touch screens, solar cells and light-emitting devices. In present, TCO films such as tin-doped indium oxide (ITO), aluminum-doped zinc oxide (AZO) and fluorine doped SnO_2 (FTO) are the most widely used transparent electrodes in these devices. However, the manufacturing of ITO film requires precious raw materials indium and other TCO films still have to improve their conductivity and transmittance in visible region. Moreover, due to the inherent brittleness of oxide materials, the flexibilities of TCO films are poor, which could not meet the application requirements of flexible electronics. More and more researchers are focusing on finding new transparent conductive materials as substitutes.

Multilayer composite TCFs based on ultrathin metal film exhibit high conductivity, good transparency and excellent flexibility. In this feature article, we review the recent progress of multilayer composite TCFs with dielectric/metal/dielectric (DMD) structure by describing the basic principles, the materials and thickness selection of each layer, the structural types, the methods of photoelectric performance improvement, and other important properties of multilayer composite TCFs with the DMD structure.

Due to the good conductivity and ductility of metal layers, multilayer composite TCFs with the DMD structure show low sheet resistance and excellent mechanical flexibility. Some metals such as Ag, Au, Cu, Al, Pd, Pt, Mo, Ni, In and metal alloys have been used as the metal interlayer of DMD electrodes. Among them, the most frequently used metals are Ag, Cu and Au. The two dielectric layers in DMD electrodes may be utilized to improve the overall transmittance in the visible spectral range by optical interference within the multilayer structure, while their thickness can be chosen as a function of the device properties requested. As the metal provides a high lateral conductivity, the dielectric layers in the DMD electrodes do not require being highly conductive, therefore they can be selected in a wide range of materials such as ITO, AZO, FTO, MoO_3 , WO_3 , TiO_2 , ZnS, etc. Experimental data have shown that the same transmittance and sheet resistance values could be obtained with DMD structures composed of different dielectric and metal combinations. In addition, high temperature deposition and annealing are not required to achieve good electrical conductivity, in spite of the higher resistivity achieved by dielectric films prepared without heating. Therefore, DMD electrodes are suitable to deposit onto unheated plastic substrates by continuous roll-to-roll techniques.

The efficiencies of DMD electrodes are seriously constrained by a deleterious trade-off between the optical transmittances and electrical conductivities of the metal layers. An improvement in the electrical conductivity requires an increase in the thickness of the metal layer, but the increase of thickness seriously reduces the transmittance. Moreover, due to the three dimensional island growth mode of metal layers deposited using vacuum coating techniques, the metal film usually has a threshold thickness that is the minimum possible thickness for forming a continuous layer to provide sufficient electrical paths. Below the threshold thickness, both the electrical resistivity and the optical absorption rapidly increase. The conductivity and transmittance of a thin metal layer are normally optimized at or near the percolation threshold thickness, since a high optical transmission is required in most cases. Therefore, reducing the percolation threshold thickness of metal layers is a key to improve their conductivity and transmittance simultaneously. In the latest years, some impressive improvements have been achieved by controlling the underlay material, seed layer, dopants and deposition rate at the deposition of metal layer.

So far, multilayer composite TCFs with the DMD structure have primarily been applied in solar cell and light-emitting devices, where multilayer composite TCFs may be used as cathodes or anodes, even intermediate electrodes due to the electrode work function easily adjusted by the selection of dielectric layer material. When the multilayer electrodes are applied in solar cell, higher power conversion efficiencies have been achieved compared with devices fabricated on single-layer TCO electrodes. Although there are some challenges yet to overcome to optimize the processing and performance of multilayer composite TCFs, multilayer composite TCFs with the DMD structure remain a highly suitable candidate for various flexible electronic applications in the near future.

transparent conductive film, dielectric/metal/dielectric, multilayer composite, ultrathin metal film, flexibility

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