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高分子基金属复合材料的前沿应用

张梦飞 张久洋*
(东南大学化学化工学院,南京 210023)

摘 要 高分子基金属复合材料作为一种具有独特物理属性的功能材料,兼具金属的高导电导热性以及加工便利性。近年来,高分子基金属复合材料成为科技前沿热点。复合材料不仅在芯片堆叠、集成电路和系统集成等高精度封装中实现技术突破,而且为医疗传感装置、柔性显示屏和软体机器人的开发提供了新思路。本文系统介绍了高分子基金属复合材料,从工作性能、应用概况及市场分析等方面总结其在电子封装、柔性显示、医疗传感和电磁屏蔽领域的的研究现状。

关键词 高分子基金属复合材料;电子封装;柔性电子;电磁屏蔽
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从青铜时代到陶瓷时代,材料的更迭折射出人类智慧的光芒。现如今电子信息的飞速发展则对材料提出了高层次要求,高分子基金属复合材料凭借优异光电性能、机械稳定性及低成本特点,其未来应用价值很高(图1)[1-6],有望助力电子封装、柔性传感、电磁屏蔽等诸多先进电子领域的蓬勃发展。

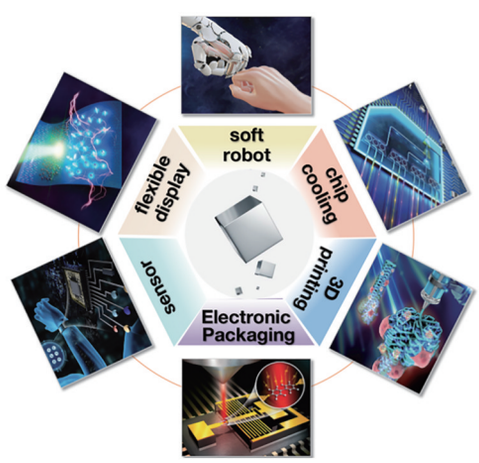

图1 高分子基金属复合材料在先进电子领域的应用方向[1-6]

Fig. 1 The application direction of polymer-based metal composites in the field of advanced electronics[1-6]

1 电子封装领域

电子封装是一门研究微电子产品制造的科学与技术,通俗讲是将设计好的电子芯片、电路用特定的封装材料连接,是产品生产的重要环节。随着数字信息的爆炸性增长,封装要求也不断向着小型化、高导热和高密集度方向发展[7]。

近年来相关研究持续推进,不仅在工艺上从最初的系统级封装、封装体叠层技术(Pacage-on-package, POP)发展到3D集成电路堆叠[8]和扇出封装[9],材料上的选择也进一步更新。早期以陶瓷封装为主,但其成本高昂、工艺自动化能力差且难以满足高精度封装,因此需要开发出成本低廉的塑料封装,

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*E-mail: jiuyang@seu.edu.cn

目前，塑料封装占据集成电路封装市场的95%，但传统塑封一度使用锡铅焊料，存在具有很大弊端[10]。首先，只能应用于0.65 mm以上节距的连接，大大制约封装精度。其次，高于230 ℃产生的热应力会对基板造成损伤，造成污染，不适合大规模的推广应用，为此，急需寻找替代材料[11-12]。

将金、银、铜和镍等金属掺杂到环氧树脂、丙烯酸酯树脂以及聚氯酯等高分子基体中[13-14]，在克服传统金属加工性差，高成本且易腐蚀等缺点的同时，赋予材料流动性，可制成导电膜、导电粘合剂，在尖端市场发展迅速[15-16]，潜在应用市场巨大(高分子基金属复合材料的基本性能和潜在应用见图2，图片来源于电子发烧网)。目前，美国Kemtron和3M公司制备的异方导电胶具有高分辨率(可满足小于50 μm的沟道)、快速处理和低工艺温度等优势，几乎占据了所有的集成电路和发光二极管领域，产品应用于液晶显示模组、液晶驱动模组、摄像头模组、柔性电路板、触控屏连接线、高精密排线和集成电路的制造中。为加大国际市场占有率，我国科研团队不断钻研创新，作者团队等将低熔点液态金属与胶粘剂结合制得的各向异性导电胶，通过在加热到特定温度施加外力，实现3D空间上的导电差异性，开辟了各向异性导电胶的新思路。但目前全面工业化应用还面临着高键合压力、位置放置以及材料对环境湿度的敏感性等问题，需要进一步深入研究。

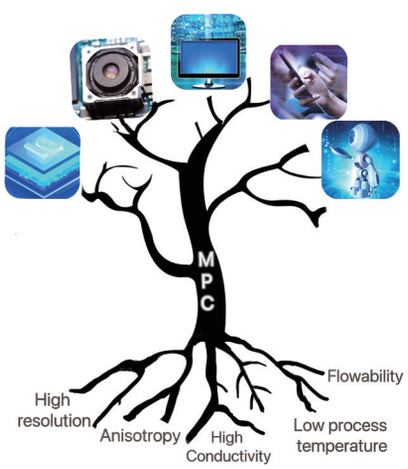

图2 高分子基金属复合材料在电子封装领域的基本性能与潜在应用(图片来源于电子发烧网：https://www.elecfans.com)

Fig. 2 Basic performance and potential applications of polymer based metal composites in the field of electronic packaging (Image from Electronic Fever Network: https://www.elecfans.com)

电子封装另一研究热点便是绝缘导热封装[17]，高分子材料凭借低成本和优良电绝缘性脱颖而出[18]，但大多数的聚合物本征导热性较差，无法满足特征线宽较窄的器件高频发热率，而将金属与高分子进行掺杂复合后，电热性能得到优化，大大契合高功率器件的封装需求[19]，有望解决目前散热封装市场面临的2大瓶颈：1)材料导热系数难以提高制约大功率电器及高端领域的发展，应用高导热的银铜纳米粒子复合高分子基体可赋予材料高热导率、高强度和热膨胀系数可调等优势，同时，制备过程中采取外力对粒子进行取向，可实现各向异性的热导率并降低导热逾渗阈值，采取纳米级别微粒调控粒子形态可处理界面复合问题[20-21]。2)导热和相变材料难以兼容，选择液态金属半固态金属制备有机复合相变材料，可以在增加导热系数的同时，赋予其优秀的光热转换能力，扩展了材料应用范围。近年来，通过共混法掺杂金属纳米粒子提高有机体导热系数，采取微胶囊法解决相变材料泄漏问题等相变材料的相关研究正不断推进。此外，从三元相图出发[22]，制备出具有持续相变能力、可调控和流动性的金属高分子硅脂，可将导热系数提高至20 W/(m·K)以上，成功实现了对现代消费电子的热控制。

人工智能、航空航天、第五代移动通信技术(5G)和柔性电子[23]等技术继续推动着后摩尔时代先进封装的发展。据知名半导体分析机构Yole数据，2021年全球先进封装市场总营收达321亿美元，预计到2027年复合年均增长率将达到10%，激增至572亿美元。与此同时，我国相关企业通过国际并购、技术

创新等途径飞速成长,其中长电科技、通富微和天水华天科技等企业在全球市场占有率和技术上已经和外资、台资头部企业达到同等水准,整体竞争实力逐渐增强,高端市场有望实现进口替代化进程

2　柔性电子领域

柔性电子是将电子元件沉积到柔性可延性基板上的一项新兴电子技术,广泛应用在医疗、人工智能和微电子等领域,相关电子产品对外形适应性和界面软性需求与日俱增,推动着柔性电子技术的飞速发展。相比于耗资高昂、生产设备庞大的硅基半导体,柔性电子凭借加工便利且变形时的高效光电性能脱颖而出,相关研究已经从起步阶段迈入实质性发展阶段,其研究热度也一直居高不下[24-26]。

柔性电子器件的结构材料可分为基底材料与功能性材料。柔性基材需要具备实现特定需求的形状、承受复杂机械变形及受损后可以自我修复等特点,常见的柔性基材有聚酰亚胺、聚乙烯醇、聚酯和聚萘二甲酯乙二醇酯等。用于柔性电子功能材料主要有有机材料、无机半导体材料[27]、碳材料[28]和金属材料[29]等。其中,以聚苯胺聚噻吩为代表的有机材料表现出优异的热电性能和电学传输性能[30],且密度低、易加工可掺杂,常用于有机LED,有机薄膜晶体管和柔性超级电容器中,但也存在载流子传输需求(高度规整连端排列)与柔性需求(高链段自由度)难以兼顾的弊端。碳纳米管、石墨烯等碳基材料[31-33]具有优异的机械性能、光电特性,在应用时显示出高载流子迁移率,但难以避免脆性大和高温易氧化的缺点。相比之下,选择合适金属复合可实现材料的柔性导电化,广泛应用这一领域固态金属大多以纳米颗粒和纳米线的形式存在,特别是银纳米线凭借良好的化学、机械和导电稳定性以及光学透明性实现了诸多应用。除了传统固态金属,液态金属受益于金属与流体之间的相互结合兼顾了变形性和导电性,在柔性电子领域应用中,大放光彩。

选择可承受近乎无限应变的液态金属与弹性体进行设计复合,可解决刚性电子元件中缺乏延展性易导致材料分层或局部断裂的问题,相比于碳纳米管石墨烯有机半导体等柔性传感器,液态金属柔性传感器可克服高应变下性能不稳定性,从而拓宽了应用范围,在减小迟滞的同时,保证拉伸性,为可穿戴设备、电子皮肤和软机器人的蓬勃发展助力[34-35]。液态金属柔性导电材料目前可通过光刻技术、3D打印和注射微通道等多种复合途径加以制备[36-38]。柔性传感器的机械特性则由封装的弹性体决定,通过液态金属的形态及分布调节电性能,可设计开发出高灵敏度可回收的柔性器件[39],已经用于医疗检测、表情识别和运动监测等多领域[40-41],但要由研究阶段迈向传感领域的大规模产业化,仍面临高表面张力及泄漏问题,未来应优化加工过程以降低成本。

近年来,柔性电子产品市场稳步增长,据弗若斯特沙利文报告显示,2019年全球柔性电子市场规模达到14.2亿美元,预计到2025年全球柔性电子市场规模将达到3049.4亿美元,市场前景一片盎然(柔性电子产业结构分布图见图3,资料来源:普华有策)[42]。以纳米银线为代表的新型金属聚合物复合材料正攻占市场,为触控屏、柔性OLED、太阳能电池和智能窗膜等下游产业提供材料支持,美国Cambrios公司占有较大的先发优势,现已给三星、LG和苹果等高端品牌量产供货。国内微晶科技、深圳华科创智深耕产业线,致力向高端市场进攻,相信在未来金属聚合物复合材料也必将为柔性电子注入强大动力。

3　电磁屏蔽领域

电磁屏蔽是指利用屏蔽材料的吸收和反射等作用对电磁波进行衰减,在电子原件装配、智能隐形设备、可穿戴织物等中均有重要应用[43]。相比于易团聚的碳材料,易于腐蚀的纯金属材料和制备繁杂的导电聚合物材料,金属聚合物复合材料性能优越且兼顾机械性能,并通过掺杂调控可使屏蔽区域更加广泛[44-45]。在该类材料中,金属填料主要以Fe、Ni提供磁性能,Ag、Cu提供电性能[46],高分子材料作为复合材料的基体,提供多层对电磁屏蔽有益结构等[47]。在制备过程中充分利用粒子的各向异性,采取电镀化学镀等多种复合策略,同时编制层状、链状和网络状等多种结构[48]均可进一步提升屏蔽性能,生产的屏蔽材料现已应用在通讯设备、手机终端、汽车电子和国防军工等领域。

目前,电磁屏蔽领域已经形成了相对比较稳定的市场竞争格局,国外领先企业美国Laird、Chomerics公司等,产品范围较广占据大量高端市场。 国内绝大多数企业品种少,同质性强,未形成产品的系列化

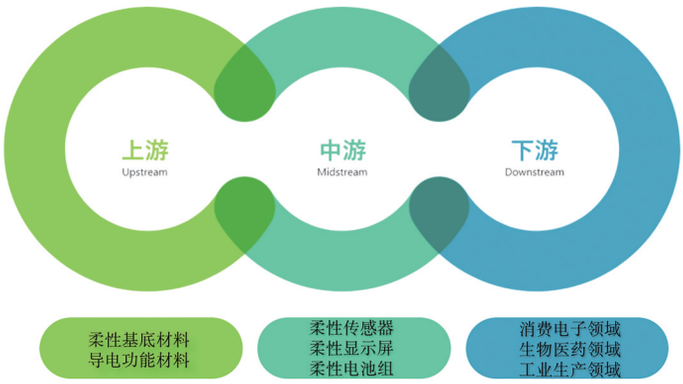

图3 柔性电子产业结构分布图(资料来源:普华有策)[42]

Fig. 3 Structural distribution of flexible electronics industry(Data source: Puhua Youce)[42]

和产业化,少数企业例如深圳飞荣达、北京中石科技通过加大对技术领域的投资逐渐具备了自主研发和生产中高端产品的能力,仍需着重解决加工过程的成本问题以及苛刻环境下的适配性问题。

4 结 论

金属高分子复合材料作为新一代绿色高效的新型复合材料,其性能与金属种类、尺寸形貌和复合工艺息息相关。目前,国内在此领域的研究仍落后于国外先进水平,对于新材料的开发与改性研究有所欠缺,界面匹配与成本性有待提高,但相信随着未来对纳米尺寸效应、性能表征及复合策略的深入研究,金属聚合物复合材料将成为数字信息化时代重要的基础电子材料。

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Frontier Applications of Polymer-Metal Composites

ZHANG Meng-Fei, ZHANG Jiu-Yang*
(*College of Chemistry and Chemical Engineering*, *Southeast University*, *Nanjing* 210023, *China*)

Abstract Polymer-metal composites are functional materials with unique physical properties, combining the high conductivity and thermal conductivity of metals with the convenient processability of polymers. In recent years, polymer-metal composites have become a hot topic at the forefront of technology. These composite materials have not only achieved technological breakthroughs in high-precision packaging for chip stacking, integrated circuits, and system integration but have also provided new insights for the development of medical sensing devices, flexible displays, and soft robotics. This article provides a systematic introduction to polymer-metal composites, summarizing their research status in the fields of electronic packaging, flexible displays, medical sensing, and electromagnetic shielding, including their working performance, application overview, and market analysis.

Keywords Polymer-metal composites; Electronic packaging; Flexible electronics; Electromagnetic shielding
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