

飞秒激光诱导多壁碳纳米管与金属电极连接的实验研究

梅欢欢^{1,2,3}, 崔健磊^{1,2*}, 程杨^{1,2}, 何小桥³, 梅雪松^{1,2}

¹西安交通大学机械制造系统工程国家重点实验室, 陕西 西安 710054;

²陕西省智能机器人重点实验室, 陕西 西安 710049;

³香港城市大学土木及建筑工程系, 香港 九龙 999077

摘要 碳纳米管因其独特的电学特性及一维纳米结构成为取代硅材料的重要电子材料, 利用碳纳米管制备的微米电子器件具有尺寸小、响应快、功耗低等优点, 但如何实现碳纳米管与金属电极之间可靠及有效的连接一直是构筑碳纳米管电子器件的难点与重点。针对该问题, 首先, 采用飞秒脉冲激光辐照技术诱导多壁碳纳米管与不同金属电极(金、镍)产生不同形式的连接; 然后, 通过测试互连前后多壁碳纳米管与金属电极之间的伏安特性曲线和界面接触电阻验证了该连接方法的可重复性及有效性, 为后续大规模制备高性能碳纳米管场效应晶体管提供了一定的基础。

关键词 飞秒激光; 多壁碳纳米管; 金属电极; 异质连接; 电学性能

中图分类号 TN249

文献标志码 A

doi: 10.3788/CJL202148.0802019

1 引言

自计算机和集成电路诞生以来, 半导体工业沿着摩尔定律指出的方向飞速发展。2005 年, 国际半导体技术发展路线图(ITRS)委员会明确指出 2020 年前后硅基互补金属氧化物半导体(CMOS)技术可能达到其性能极限^[1]。2008 年, ITRS 新兴研究材料和新兴研究器件工作组在考察所有可能的硅基 CMOS 替代技术后, 将碳基电子学作为未来 5~10 年内的下一代电子技术, 并在 2009 年将碳基纳米材料列入延续摩尔定律的未来集成电路技术中^[2-3]。碳纳米管(CNTs)凭借其独特的电学性质和一维纳米结构, 在众多碳基材料中脱颖而出, 成为国内外科学家关注和研究的焦点^[4-5]。强共价键结构使 CNTs 具有较高的机械稳定性和热稳定性, 良好的抗电迁移能力使 CNTs 可承受较高的电流密度, 这些特点使 CNTs 在场效应晶体管、新型传感器和互

连导线等领域有很好的应用前景^[6-9]。在实际应用中, CNTs 与金属结构需要形成牢靠和稳定的接触才能保证器件的性能, 因此, 优化 CNTs 与金属电极之间的接触对提高基于 CNTs 器件的性能具有重要意义^[10-12]。

为了实现 CNTs 与金属电极之间有效且可靠的连接, 国内外研究学者提出了一系列连接技术, 如金属焊接法^[13]、局部退火法^[14-16]、超声焊接法^[17-18]、电子束或离子束辐照技术^[19-20]。但这些技术主要是在 CNTs 与金属电极界面上涂覆金属焊料^[21]、石墨化碳^[22]、碳化氢^[23]、Au-C^[24]等焊料, 焊料在局部能量的作用下软化或融化, 使 CNTs 与金属电极产生良好的连接。上述连接工艺都比较复杂, 且需要精准定位。此外, 焊料元素的引入会对连接性能产生一定的影响。超声焊接法虽然能很好地实现 CNTs 与多种金属电极之间牢靠的连接, 但其超声头与金属电极需要接触传递振动, 会对金属电极表面结构

收稿日期: 2020-12-01; 修回日期: 2021-01-04; 录用日期: 2021-02-23

基金项目: 国家重点研发计划(2017YFB1104900)、国家自然科学基金(52022078, 51875450)、陕西省重点研发计划(2019ZDLGY01-09)

*E-mail: cjlxjtu@mail.xjtu.edu.cn

造成不可逆转的损伤。因此,亟需寻求一种工艺简单、且需在不破坏金属电极或其他结构的前提下能大规模实现的连接技术。激光加工技术具有峰值功率高、非接触加工、可控性好等优点,被广泛应用于电子器件的制造中。其中,飞秒脉冲激光的脉宽小于电子冷却时间,被认为是一种冷加工技术,可以很好地避免热累积对金属电极结构的破坏^[25],是一种理想的高能束互连技术。

本文利用飞秒脉冲激光辐照方法系统地研究了激光辐照时长等激光参数对多壁碳纳米管(MWCNTs)形貌、金属电极结构的影响规律,实现了MWCNTs与不同金属电极(金、镍)之间良好的连接,并通过电学性能测试实验验证了MWCNTs与金属电极之间连接的有效性及其可重复性。

2 实验装置和方法

作为飞秒脉冲激光诱导CNTs-金属电极连接实验中的关键部件,飞秒脉冲激光器的性能参数是决定连接效果的关键。实验选用的激光器为美国Newport Corporation公司生产的SPFIRE ACE-100F1K型激光器,其重复频率为1 kHz、脉冲宽度为120 fs、中心波长为800 nm,具体实验装置如图1所示。用功率计实时监测激光的脉冲能量,并通过焦距为50 mm的柱面镜将光束聚焦在样品表面,在焦点处对电极边缘及其与MWCNTs相互接触的部位进行辐照。用同轴照明激光和CCD相机对金属电极进行简单定位,用电脑控制快门和三维(3D)电控移动平台。

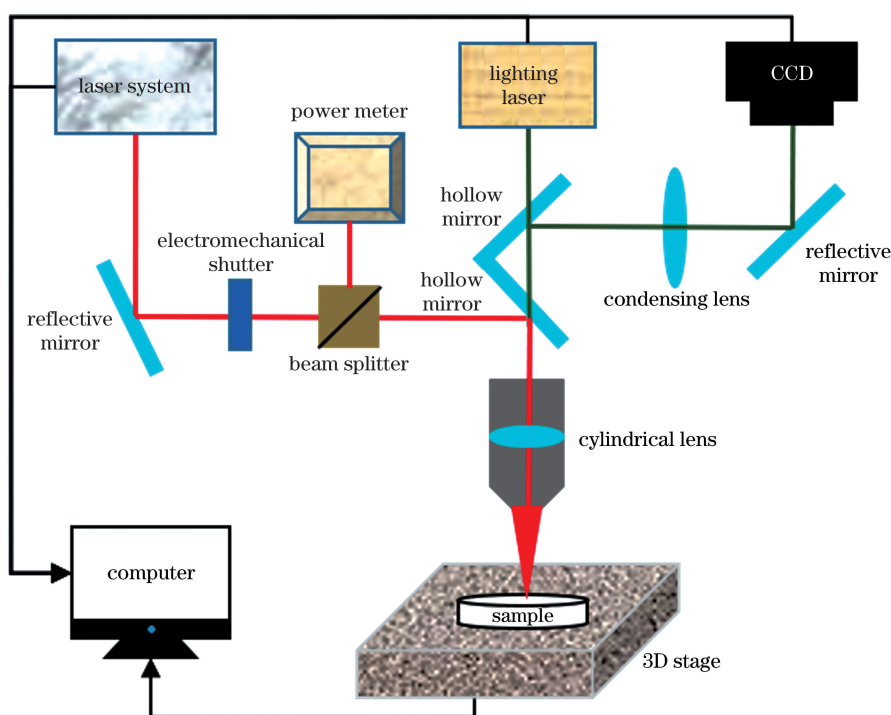


图 1 实验装置图

Fig. 1 Diagram of the experimental setup

实验采用的MWCNTs粉末采购于中国南京先丰公司,标称纯度大于70%,直径为30~50 nm,长度为5~10 μm 。MWCNTs分散的均匀性和稳定性直接影响到MWCNTs实际应用的性能,实验首先用质量浓度为0.1 mg/mL的十二烷基硫酸钠(SDS)作为表面活性剂,然后结合超声振动实现MWCNTs在水溶液中的均匀稳定分散。为了直观观测到MWCNTs和金属之间的接触情况,先利用光刻技术铺设电极,再用旋涂工艺沉积MWCNTs。该过程中金属电极不仅是MWCNTs的载体,也是

后续电学性能测试时测试探针的载体,因此金属电极需要具备较大的面积(大于 $100\ \mu\text{m} \times 100\ \mu\text{m}$)和较小的沟道宽度(小于 $10\ \mu\text{m}$),以实现MWCNTs和金属电极、探针与金属电极的接触。同时,还需要考虑电极尺寸的影响。电极太厚会使光刻过程中部分图形无法从表面剥离,电极太薄会使MWCNTs难以埋入金属电极中。针对上述要求,设计出的矩形电极形貌如图2(a)所示,该电极的尺寸为 $200\ \mu\text{m} \times 200\ \mu\text{m}$,中间沟道宽度为 $8\ \mu\text{m}$ 。通过光刻工艺得到符合要求的电极组,如图2(b)所示。

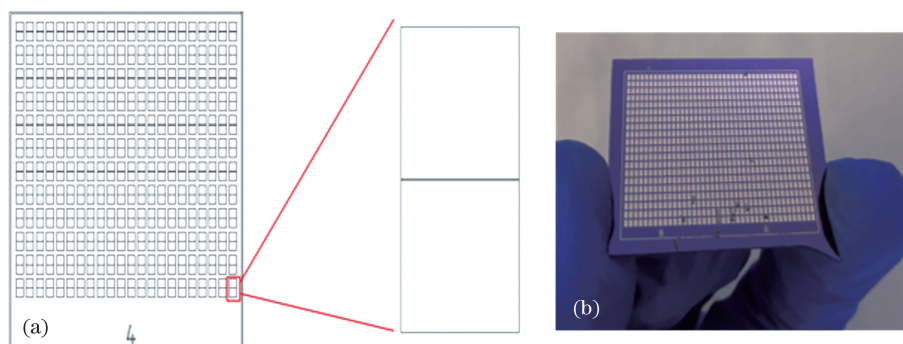


图 2 光刻工艺制备的电极。(a)电极图案;(b)电极矩阵的实物图

Fig. 2 Electrodes prepared by photolithography process. (a) Electrode pattern; (b) physical image of the electrode matrix

铺设好金属电极后,采用旋涂工艺将 MWCNTs 沉积到电极上,使 MWCNTs 和金属电极之间形成物理接触。MWCNTs 的质量浓度决定了电极上沉积 MWCNTs 的密度和数量,当 MWCNTs 的质量浓度过低时,MWCNTs 沉积在金属边缘处的概率较低,导致后续连接和观测困难;当 MWCNTs 的质量浓度过高时,沉积在金属电极上的 MWCNTs 直接形成致密薄膜,且会产生多层重叠现象,阻碍飞秒激光辐照到金属表面,影响实验结果。因此对不同质量浓度 MWCNTs 分散液的沉积效果进行了对比实验,结果如图 3 所示。

可以发现,当质量浓度为 0.03 mg/mL 和 0.01 mg/mL 时,多层 MWCNTs 沉积在一起,数量和密度过大,不利于后续实验观察;当质量浓度为 0.005 mg/mL 时,MWCNTs 的数量和密度适中。因此实验采用质量浓度为 0.005 mg/mL 的 MWCNTs 分散液将 MWCNTs 沉积在金属电极上,并用扫描电子显微镜 SEM (Hitachi, SU-8010) 表征分散的 MWCNTs 本征结构、金属电极结构、MWCNTs-金属电极形貌,用半导体器件分析仪 (Keysight, B1500A) 测试互连前后 MWCNTs 和金属电极之间的电学性能。

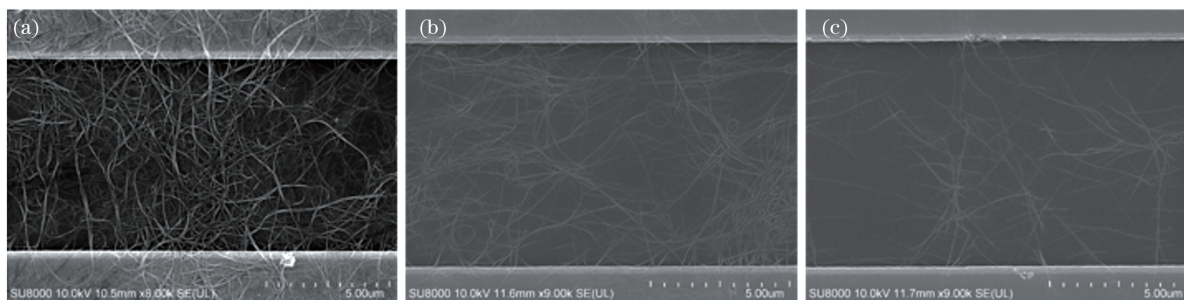


图 3 不同质量浓度的 MWCNTs 溶液沉积效果图。(a) 0.03 mg/mL;(b) 0.01 mg/mL;(c) 0.005 mg/mL

Fig. 3 Deposition effect images of the MWCNTs solution with different mass concentrations. (a) 0.03 mg/mL; (b) 0.01 mg/mL; (c) 0.005 mg/mL

3 实验结果及分析

3.1 Au 电极与 MWCNTs 的连接

飞秒脉冲激光诱导 MWCNTs 与金属电极之间连接的效果,与激光参数(如激光辐照方式、激光功率、辐照时长)有密切联系,为了简化激光参数的变化对实验结果的影响,采用定点辐照方式进行连接实验。定点辐照是激光和样品保持相对静止,以固定的激光功率和时间辐照样品,使 MWCNTs 与金属电极连接处的形貌发生变化。图 4 为飞秒脉冲激光功率为 220 mW 时,不同辐照时长下 MWCNTs-Au 电极

的 SEM 图像,其中,Au 电极的厚度为 200 nm。

从图 4 可以发现,当激光辐照时长为 30 s 时,Au 电极表面的 MWCNTs 管状结构清晰可见,MWCNTs 仅搭接在 Au 电极表面;当辐照时长为 60 s 时,MWCNTs 的一端与 Au 电极表面产生连接,如图 4(b)中箭头所示的位置,且 MWCNTs 管壁有褶皱;当辐照时长增加到 61 s 时,Au 电极表面的 MWCNTs 基本被激光打飞,且电极表面结构遭到严重破坏。当飞秒激光辐照时长较短时,由飞秒脉冲激光在金属电极表面激发的等离子形成的电场强度和两种材料之间形成的局部近场增强效应都不

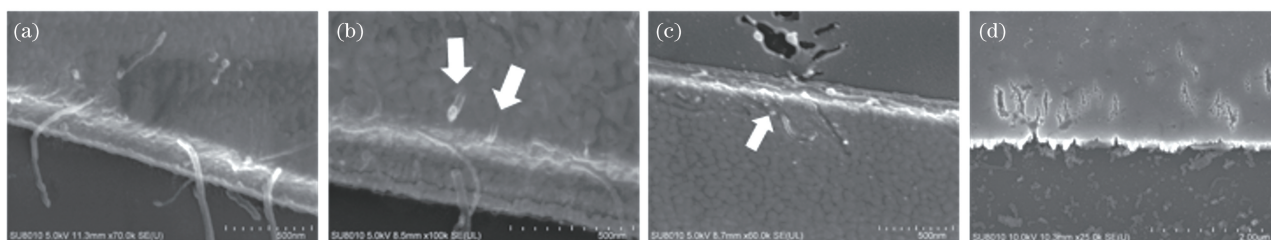


图 4 不同辐照时长下 MWCNTs-Au 电极的 SEM 图像。(a) 30 s; (b) 60 s; (c) 61 s; (d) 65 s

Fig. 4 SEM images of the MWCNTs-Au electrode at different irradiation time. (a) 30 s; (b) 60 s; (c) 61 s; (d) 65 s

足以让 Au 电极表面产生变化,此时 MWCNTs 和 Au 电极始终保持搭接状态。随着辐照时长的增加,Au 电极与 MWCNTs 相互接触区域的近场增强效应进一步加强,使相互接触的区域发生了改性,MWCNTs 一端被埋入金属电极内部,形成了较好的连接。当辐照时长持续增加,其表面产生的近场增强效应直接破坏了 Au 电极的表面结构,且 MWCNTs 在飞秒脉冲激光冲击波的作用下从金属电极表面被移除。Au 电极与 MWCNTs 形成连接时的理想激光功率和辐照时长,应该是飞秒脉冲激光的局部近场增强效应下,接近 Au 电极表面出现微熔融状态而不出现烧蚀现象对应参数的下极限。图 5 为 Au 基底烧蚀时飞秒脉冲激光辐照时长随激

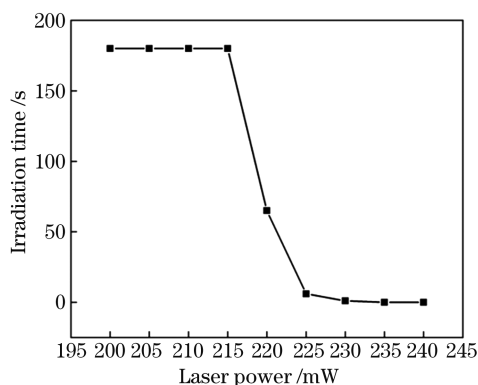


图 5 烧蚀 Au 基底时辐照时长随激光功率的变化曲线

Fig. 5 Variation curve of the irradiation time with laser power when ablating Au substrate

光功率的变化趋势,可以发现,激光功率与辐照时长并非线性关系,而是分为三个阶段。第一个阶段是非作用阶段,在该阶段内增加激光辐照时长对 Au 电极表面的影响可以忽略不计。第二个阶段是选择性改性阶段,当激光功率增加到 220 mW、辐照时长为 60 s 时,MWCNTs 与 Au 电极表面之间的局部等离子体增强效应使金属表面发生了改性。当飞秒脉冲激光辐照到 Au 电极表面时,Au 原子中的自由电子与激光光子发生了非弹性碰撞,吸收光子能量的自由电子向高能级跃迁,增加了晶格的热震荡,使局部区域升温、软化,进而形成微熔池;在激光光压下 MWCNTs 被埋入金属电极中,形成了良好的嵌入式连接。当激光能量为 220 mW、辐照时长为 65 s 时,Au 电极表面会出现大面积烧蚀现象。第三个阶段为材料去除阶段,当激光功率增加到 235 mW 时,金属电极表面在辐照时长为 50 ms 时就出现了不同程度的损坏及烧蚀等现象。

3.2 Ni 电极与 MWCNTs 的连接

为了验证 MWCNTs 能够与不同金属电极产生连接,采用与 3.1 小节相同的光刻工艺,制备了厚度为 100 nm 的金属 Ni 电极,图 6 为金属 Ni 电极与 MWCNTs 在激光功率为 28 mW 时不同辐照时长下的 SEM 图像。可以发现,当辐照时长为 30 s 或更短时,MWCNTs 能保持较好的管状结构,金属电极表面的结构基本完整,MWCNTs 仅依靠范德华力与金属基底接触。当辐照时长增加到 60 s 时,

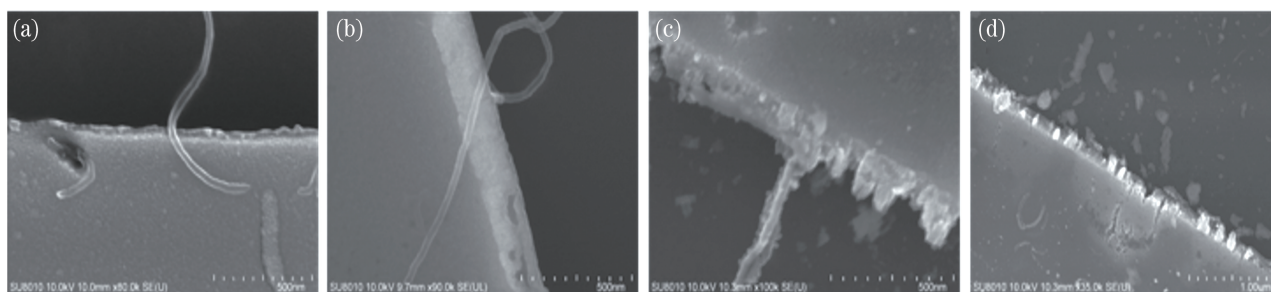


图 6 不同辐照时长下 MWCNTs-Ni 电极的 SEM 图像。(a) 30 s; (b) 60 s; (c) 61 s; (d) 65 s

Fig. 6 SEM images of the MWCNTs-Ni electrode at different irradiation time. (a) 30 s; (b) 60 s; (c) 61 s; (d) 65 s

MWCNTs 的一端和 Ni 电极之间产生了连接,其连接处的 MWCNTs 直径略大于未参与连接的 MWCNTs 直径。当辐照时长增加到 61 s 时, MWCNTs 的一端与金属电极之间产生了紧密连接,且金属电极表面在激光作用发生了烧蚀现象, Ni 电极的飞溅物包裹了 MWCNTs。当辐照时长继续增加时, Ni 电极边缘区的结构被完全破坏,沉积在 Ni 电极上的 MWCNTs 完全被剥离。

图 7 为烧蚀 Ni 基底时辐照时长随激光功率的变化曲线,可以发现,其变化趋势与烧蚀 Au 基底时基本相同,也可大致分为三个阶段。在非烧蚀阶段, MWCNTs 与金属基底通过范德华力接触, MWCNTs 的形貌与电极结构完整。在选择性改性阶段, MWCNTs 仍保持其本征结构,在激光作用下 MWCNT 的一端与金属 Ni 产生了包覆性连接。辐照时长持续增加时, Ni 电极在激光作用下产生了烧蚀现象,沉积在电极表面的大部分 MWCNTs 被剥离。

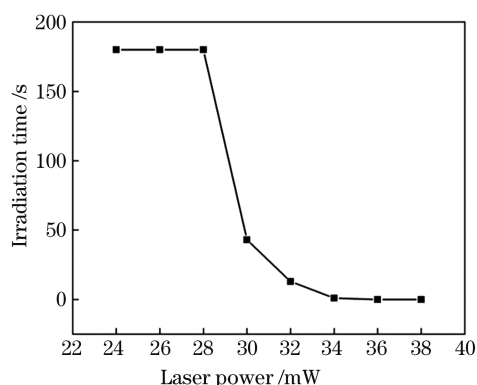


图 7 烧蚀 Ni 基底时辐照时长随激光功率变化曲线

Fig. 7 Variation curve of the irradiation time with laser power when ablating Ni substrate

MWCNTs 与金属电极的位置^[26-27]、金属的润湿特性及碳原子的结合力^[28-29]对两者的连接形式有很大影响,且 MWCNTs 管壁上的强共价键会在激光作用下被破坏,形成空位与缺陷,而空位与缺陷容易在外界能量作用下与金属电极之间形成牢靠的共价键^[30-31]。在飞秒脉冲激光辐照下,金属电极与 MWCNTs 相互接触的区域产生了局部近场增强效应,金属 Ni 电极表层的自由电子吸收激光能量,形成超热电子。超热电子迅速向四周扩散,通过电子-声子耦合将能量传递给 Ni 原子,使 Ni 原子具有较大的动能。与此同时, MWCNTs 与金属电极形成了端点接触,其 MWCNTs 端口的碳原子环对 Ni 原子产生的吸附力^[32],使 Ni 原子向 MWCNTs 表面

迁移,对 MWCNTs 形成了包覆。这种连接形式最直接的表现是金属电极与 MWCNT 连接处的 MWCNTs 直径比未发生连接的 MWCNT 直径略大。Ni 金属 d 轨道上有不成对的电子与碳原子 2p 轨道在外界能量的作用下可进行杂化,形成较强(每个 Ni 原子的结合能可达 2.0 eV)的共价连接^[33]。Au 金属对 CNTs 的润湿性比 Ni 金属对 CNTs 的润湿性差,因此 Au 金属在 CNTs 上不能形成金属层,只能形成一个个孤立的金属岛^[33],且 Au 金属 d 轨道完全被电子占据,很难通过杂化与 CNTs 之间形成较强的(每个 Au 原子的结合能小于 1.0 eV)的连接。因此当飞秒脉冲激光与 Au 电极相互作用时, MWCNTs 与 Au 电极之间产生的近场增强效应使与 MWCNTs 接触的 Au 电极表面迅速升温软化,将 MWCNT 的一端或整根 MWCNT 埋入 Au 电极,形成嵌入式连接。

3.3 电学性能测试

为了研究 MWCNTs 与金属电极被激光辐照前后的电学性能变化,分别测试了 MWCNTs 与 Au、Ni 电极结构中两电极间两点的伏安特性曲线及相应的界面电阻。对于金属-MWCNTs-金属结构,其总电阻 R 由金属电极本征电阻 R_1 、MWCNTs 本征电阻 R_2 、MWCNTs 和金属电极接触电阻 R_3 组成。金属电极和 MWCNTs 都是较好的导体,其激光辐照前后的电阻变化可忽略不计,因此辐照前后的电阻变化量 ΔR 约等于 ΔR_3 。图 8 为飞秒脉冲激光辐照金属电极和 MWCNTs 前后同一组样品的电流-电压(I - V)曲线,激光辐照时长均为 60 s,激光功率分别为 220 mW (Au-MWCNTs)、28 mW (Ni-MWCNTs)。可以发现,相比辐照前,辐照后的接触电阻均有大幅度下降。计算结果表明,当电压为 5 V 时, Au-MWCNTs 之间的接触电阻从 454.22 k Ω 下降至 79.80 k Ω , Ni-MWCNTs 之间的接触电阻从 505.77 k Ω 下降至 36.4 k Ω ,这表明飞秒脉冲激光辐照后金属-MWCNTs 结构的电学性能有明显提升,其界面的接触电阻也有大幅度降低。

为了更具体地对比辐照前后金属电极与 MWCNTs 界面接触电阻的变化,分别给出了 10 组 Au-MWCNTs 和 Ni-MWCNTs 辐照前后的电阻变化结果,如图 9 所示。可以发现,飞秒激光辐照前,两种结构的界面接触电阻均为 500 k Ω 左右。界面接触电阻较大的主要原因是金属电极制备或 MWCNTs 沉积过程中其表面和界面附着了污染物,此外, MWCNTs 与金属电极之间的有效接触面

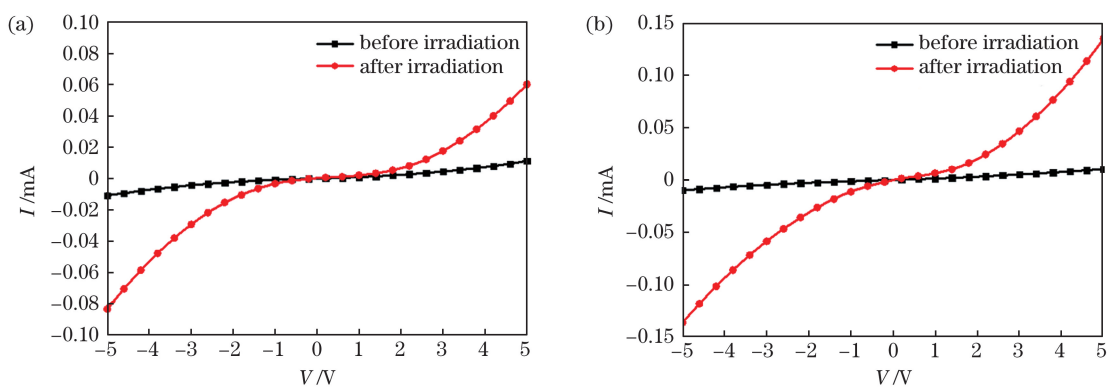
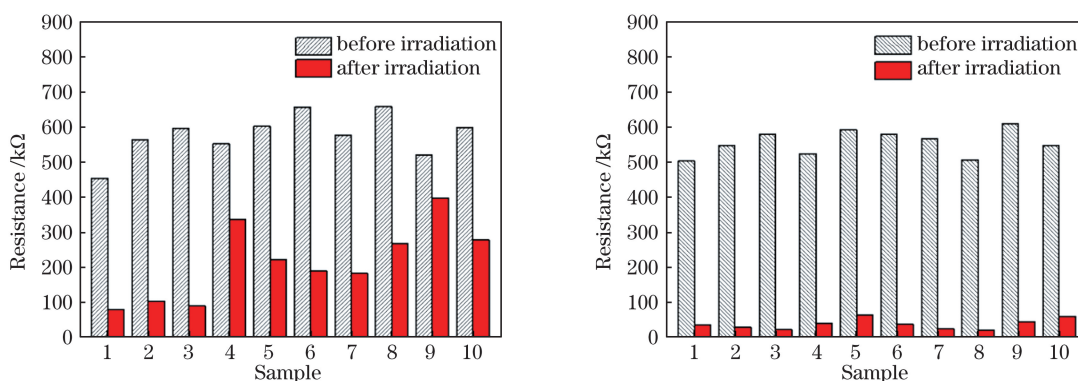
图 8 同一样品辐照前后的 I - V 曲线。(a) Au-MWCNTs; (b) Ni-MWCNTsFig. 8 I - V curves of the same sample before and after irradiation. (a) Au-MWCNTs; (b) Ni-MWCNTs

图 9 不同样品辐照前后的界面接触电阻变化曲线。(a) Au-MWCNTs; (b) Ni-MWCNTs

Fig. 9 Change curves of the interface contact resistance before and after irradiation for different samples.

(a) Au-MWCNTs; (b) Ni-MWCNTs

积较小,影响了电子输运。飞秒激光辐照后, Au-MWCNTs-Au 和 Ni-MWCNTs-Ni 结构的界面接触电阻均有大幅度减少。Au-MWCNTs-Au 结构的接触电阻从 454~658 k Ω 下降到 78.9~397 k Ω , Ni-MWCNTs-Ni 结构的接触电阻从 505~612 k Ω 下降到 21.1~64.6 k Ω 。MWCNTs 表面对 Au 原子的吸附能力较弱,使 MWCNTs 在 Au 电极表面形成较弱的粘结界, Au-MWCNTs-Au 结构仍具有较大的界面接触电阻。而 MWCNTs 对 Ni 金属的吸附能力较强,可以在金属表面形成较强的粘结界面^[32-33], 相比 Au-MWCNTs-Au 结构, Ni-MWCNTs-Ni 的界面接触电阻较小,因此激光辐照前 Au-MWCNTs-Au 结构的平均界面接触电阻略高于 Ni-MWCNTs-Ni 结构的平均界面接触电阻。当 MWCNTs 与金属电极产生连接后,连接过程中激光产生的热会稀释或分解界面处的污染物,减少由外界污染导致的接触电阻。从微观结构来看, Au-MWCNTs-Au 和 Ni-MWCNTs-Ni 结构中,金属 Au 和 MWCNTs 之间形成的嵌入式连接,金属 Ni 与 MWCNTs 之间形成的包覆式连接,均能增加

电子的输运通道,使接触电阻大幅度减小,从而增加其导电能力。

4 结 论

通过实验研究了飞秒脉冲激光的加工参数如辐照时长、激光功率对不同金属电极与 MWCNTs 连接的影响,通过观测 MWCNTs 本征结构、MWCNTs-金属电极之间的相貌变化、金属电极边缘结构变化确定了最佳连接工艺参数。当激光功率为 220 mW,辐照时长为 30 s 时, Au 电极与 MWCNTs 之间形成嵌入式连接;当激光功率为 28 mW,辐照时长为 30 s 时, Ni 电极与 MWCNTs 形成包覆式连接。在相同激光功率下继续增加辐照时长,会使金属电极表面发生烧蚀,电极边缘结构被破坏,沉积在电极表面的 MWCNTs 也会在激光的冲击波下被剥离,无法形成良好的连接。后续的电学性能测试结果表明,不同样品的电阻下降趋势基本相同,验证了该连接的可重复性。Au-MWCNTs-Au 结构的接触电阻从 454~658 k Ω 下降到 78.9~397 k Ω , Ni-MWCNTs-Ni 结构的接触电阻从 505~

612 k Ω 下降到 21.1~64.6 k Ω ,验证了该连接的有效性,也表明金属对 MWCNTs 的结合力及润湿性对其互连前后的电子运输有一定程度的影响。

参 考 文 献

- [1] Allan A. International technology roadmap for semiconductors (ITRS) [J]. *Journal of Applied Physics*, 2015, 86(17): 045406.
- [2] Khan H N, Hounshell D A, Fuchs E R H. Science and research policy at the end of Moore's law [J]. *Nature Electronics*, 2018, 1(1): 14-21.
- [3] Waldrop M M. The chips are down for Moore's law [J]. *Nature*, 2016, 530(7589): 144-147.
- [4] Wu X F, Yin H L, Li Q. Femtosecond laser processing of carbon nanotubes film [J]. *Chinese Journal of Lasers*, 2019, 46(9): 0902002.
吴雪峰,尹海亮,李强.飞秒激光加工碳纳米管薄膜试验研究[J].*中国激光*, 2019, 46(9): 0902002.
- [5] Hills G, Lau C, Wright A, et al. Modern microprocessor built from complementary carbon nanotube transistors [J]. *Nature*, 2019, 572(7771): 595-602.
- [6] Franklin A D, Luisier M, Han S J, et al. Sub-10 nm carbon nanotube transistor [J]. *Nano Letters*, 2012, 12(2): 758-762.
- [7] Yang L J, Cui J L, Wang Y, et al. Research progress on the interconnection of carbon nanotubes [J]. *New Carbon Materials*, 2016, 31(1): 1-17.
杨立军,崔健磊,王扬,等.碳纳米管互连技术新进展[J].*新型炭材料*, 2016, 31(1): 1-17.
- [8] Avouris P, Chen Z H, Perebeinos V. Carbon-based electronics [J]. *Nature Nanotechnology*, 2007, 2(10): 605-615.
- [9] Cui J L, Mei H H, Zhang J W, et al. Interfacial contact behavior between CNTs and AgNW with molecular dynamics simulation [J]. *Materials*, 2020, 13(6): 1290-1296.
- [10] Chen MX, Song X H, Liu S, et al. Batch welding of aligned carbon nanotube onto metal electrodes [J]. *Microsystem Technologies*, 2012, 18(6): 679-682.
- [11] Cao Q, Han S J, Tersoff J, et al. End-bonded contacts for carbon nanotube transistors with low, size-independent resistance [J]. *Science*, 2015, 350(6256): 68-72.
- [12] Santini C A, Volodin A, van Haesendonck C, et al. Carbon nanotube-carbon nanotube contacts as an alternative towards low resistance horizontal interconnects [J]. *Carbon*, 2011, 49(12): 4004-4012.
- [13] Liebau M, Unger E, Duesberg G S, et al. Contact improvement of carbon nanotubes via electroless nickel deposition [J]. *Applied Physics A*, 2003, 77(6): 731-734.
- [14] Woo Y, Duesberg G S, Roth S. Reduced contact resistance between an individual single-walled carbon nanotube and a metal electrode by a local point annealing [J]. *Nanotechnology*, 2007, 18(9): 095203.
- [15] Karita M, Asaka K, Nakahara H, et al. In situ TEM study on the improvement of contact resistance between a carbon nanotube and metal electrodes by local melting [J]. *Surface and Interface Analysis*, 2012, 44(6): 674-677.
- [16] Karita M, Asaka K, Nakahara H, et al. In situ TEM study on changes in structure and electrical conductance of carbon nanotube-gold contact induced by local joule heating [J]. *Journal of Materials Science*, 2013, 48(2): 936-940.
- [17] Chen CX, Yan L J, Kong E S W, et al. Ultrasonic nanowelding of carbon nanotubes to metal electrodes [J]. *Nanotechnology*, 2006, 17(9): 2192-2197.
- [18] Zhao B, Wang Y F, Zhang Y F. Decrease of contact resistance at the interface of carbon nanotube/electrode by nanowelding [J]. *Electronic Materials Letters*, 2017, 13(2): 168-173.
- [19] Bachtold A, Henny M, Terrier C, et al. Contacting carbon nanotubes selectively with low-ohmic contacts for four-probe electric measurements [J]. *Applied Physics Letters*, 1998, 73(2): 274-276.
- [20] Wei B Q, Vajtai R, Ajayan P M. Reliability and current carrying capacity of carbon nanotubes [J]. *Applied Physics Letters*, 2001, 79(8): 1172-1174.
- [21] Rykaczewski K, Henry M R, Kim S K, et al. The effect of the geometry and material properties of a carbon joint produced by electron beam induced deposition on the electrical resistance of a multiwalled carbon nanotube-to-metal contact interface [J]. *Nanotechnology*, 2010, 21(3): 035202.
- [22] Kim S, Kulkarni D D, Rykaczewski K, et al. Fabrication of an UltraLow-resistance ohmic contact to MWCNT-metal interconnect using graphitic carbon by electron beam-induced deposition (EBID) [J]. *IEEE Transactions on Nanotechnology*, 2012, 11(6): 1223-1230.
- [23] Madsen D N, Møllhave K, Mateiu R, et al. Soldering of nanotubes onto microelectrodes [J]. *Nano Letters*, 2003, 3(1): 47-49.
- [24] Yu M. Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load [J]. *Science*, 2000, 287(5453): 637-640.
- [25] Yang J J. Femtosecond laser "cold" micro-machining

- and its advanced applications[J]. *Laser & Optronics Progress*, 2004, 41(3): 42-52, 57.
- 杨建军. 飞秒激光超精细“冷”加工技术及其应用(I)[J]. *激光与光电子学进展*, 2004, 41(3): 42-52, 57.
- [26] Banhart F. Interactions between metals and carbon nanotubes: at the interface between old and new materials[J]. *Nanoscale*, 2009, 1(2): 201.
- [27] Ciraci S, Dag S, Yildirim T, et al. Functionalized carbon nanotubes and device applications[J]. *Journal of Physics: Condensed Matter*, 2004, 16(29): R901-R960.
- [28] Park S, Srivastava D, Cho K. Generalized chemical reactivity of curved surfaces: carbon nanotubes[J]. *Nano Letters*, 2003, 3(9): 1273-1277.
- [29] Menon M, Andriotis A N, Froudakis G E. Curvature dependence of the metal catalyst atom interaction with carbon nanotubes walls[J]. *Chemical Physics Letters*, 2000, 320(5/6): 425-434.
- [30] Matsuda Y, Deng W Q, Goddard W A. Contact resistance properties between nanotubes and various metals from quantum mechanics[J]. *The Journal of Physical Chemistry C*, 2007, 111(29): 11113-11116.
- [31] Maiti A, Ricca A. Metal-nanotube interactions: binding energies and wetting properties[J]. *Chemical Physics Letters*, 2004, 395(1/2/3): 7-11.
- [32] Song X H, Liu S, Yan H, et al. First-principles study on effects of mechanical deformation on outer surface reactivity of carbon nanotubes[J]. *Physica E: Low-Dimensional Systems and Nanostructures*, 2009, 41(4): 626-630.
- [33] Zhang Y, Franklin N W, Chen R J, et al. Metal coating on suspended carbon nanotubes and its implication to metal-tube interaction[J]. *Chemical Physics Letters*, 2000, 331(1): 35-41.

Experimental Study on Connection Between Multiwalled Carbon Nanotubes and Metal Electrodes Under Femtosecond Laser Irradiation

Mei Huanhuan^{1,2,3}, Cui Jianlei^{1,2*}, Cheng Yang^{1,2}, He Xiaoqiao³, Mei Xuesong^{1,2}

¹ State Key Laboratory for Manufacturing System Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710054, China;

² Shaanxi Key Laboratory of Intelligent Robots, Xi'an, Shaanxi 710049, China;

³ Department of Architecture and Civil Engineering, City University of Hongkong, Kowloon, Hongkong 999077, China

Abstract

Objective Carbon nanotubes (CNTs) have become an essential electronic material to replace silicon materials in the post-Moore era due to their unique electrical properties and one-dimensional nanostructures. The micro/nano electronic devices fabricated by CNTs have the advantages of small size, high speed, and low power consumption. The type of effective method to be used to achieve a reliable and effective connection between CNTs and metal electrodes has always been a difficulty and key point in the construction of CNTs electronic devices. To achieve an effective and reliable connection between CNTs and metals, a series of connection technologies have been proposed, such as metal welding, local annealing, ultrasonic welding, electron beam, and ion irradiation. However, some additional elements, such as graphitized carbon, hydrogen, and other solders, are introduced into the interface between CNTs and metal, which affects its connection performances. The process of some methods is complicated, and they required accurate positioning. Thus, an effective and reliable connection technology between CNTs and metal electrodes on a large-scale without damaging the metal electrodes or other structures is highly needed. The laser-processing technology is widely used to manufacture electronic devices with the advantages of high peak power, noncontact processing, and good controllability. Femtosecond pulse laser is considered a cold processing technology since its pulse width is less than the cooling time of the electron. It can avoid damage to the metal electrode structure caused by heat accumulation. Besides, it is an ideal high-energy beam interconnection technology. We use femtosecond pulse laser irradiation technology to realize an effective and repeatable connection between Multi-walled CNTs (MWCNTs) and different metal electrodes (Au and Ni), which provides a certain experimental basis for subsequent large-scale preparation of high-performance CNTs field-effect transistors.

Methods In this experiment, mass concentration of 0.1 mg/mL sodium dodecyl sulfate is applied as a surfactant, and the MWCNTs powder is dispersed uniformly and stably in an aqueous solution using ultrasonic vibration. Spin coating is adopted to deposit the MWCNTs after laying electrodes. In this process, the metal electrode is the carrier

of MWCNTs and test probe in the subsequent electrical performance test. Thus, the metal electrode should have a larger area for electrical performance test and smaller channel width for MWCNTs and metal contact. The morphology and size of the electrode are designed. The electrode is a rectangle of $200\ \mu\text{m} \times 200\ \mu\text{m}$, and the channel's width is $8\ \mu\text{m}$. The required electrode group is obtained by photolithography, as shown in **Fig. 2(a)**–**Fig. 2(b)**. Further, MWCNTs are deposited on the metal electrode by the spin coating process with a mass concentration of $0.005\ \text{mg/mL}$ MWCNTs dispersion. In this experiment, scanning electron microscope is used to characterize the intrinsic structure, metal electrode structure, and metal morphology of MWCNTs. The electrical properties are tested using a semiconductor device analyzer.

Results and Discussions Femtosecond laser irradiation technology can achieve an effective and repeatable connection between MWCNTs and metal electrodes. The results show that there is no linear relationship between the laser power and irradiation time. Considering MWCNTs and Au as examples, it can be divided into three stages. The first is the nonaction stage. In this stage, even if the laser irradiation time is continually increased, the effect on the Au surface is ignored. The second is the selective modification stage. When the laser power is increased to $220\ \text{mW}$ and the irradiation time is set at $60\ \text{s}$, the local plasma enhancement effect between MWCNTs and Au surface modifies the metal surface. When laser irradiates at the Au surface, the free-electron in Au collides with the photon of laser inelastic. Then, the free-electron absorbing photon energy migrates to a high-energy level, which increases the lattice thermal shock. Further, the local area is heated and softened, and micro molten pool formed MWCNTs are “embedded” in the metal electrode, forming a good “embedded” connection (**Fig. 4(b)**). The Au electrode will be ablated at $65\ \text{s}$ in $220\ \text{mW}$. The last stage is material removal. When the laser power increases to $235\ \text{mW}$, the electrode surface will be damaged and ablated in different degrees within $50\ \text{ms}$ (**Fig. 4(d)**). The same state also occurred in the Ni-MWCNTs structure. The results of the electrical test show that the contact resistance between MWCNTs and Au or Ni has been greatly decreased (**Fig. 9**), indicating that the connection is effective and repeatable.

Conclusions The effects of processing parameters of femtosecond pulse laser, such as irradiation, time, and laser power, on the morphology of different metal electrodes and MWCNTs, are investigated experimentally. When the laser power is $220\ \text{mW}$, and irradiation time is $30\ \text{s}$, an embedded connection formed between Au and MWCNTs. When the laser power is $28\ \text{mW}$ and the irradiation time is $30\ \text{s}$, the cladding connection formed between Ni and MWCNTs. Under the same laser power, as the irradiation time continues to increase, the metal electrode surface would be ablated, and the structure of the electrode would be destroyed. The MWCNTs deposited on the electrode surface would be peeled off by the laser shock wave. The contact resistance of Au-MWCNTs-Au structure is reduced from $454\text{--}658\ \text{k}\Omega$ to $78.9\text{--}397\ \text{k}\Omega$ and that of Ni-MWCNTs-Ni structure is reduced from $505\text{--}612\ \text{k}\Omega$ to $21.1\text{--}64.6\ \text{k}\Omega$. The latter structure is reduced by an order of magnitude, verifying the effectiveness of the connection. It also show that the bonding force and wettability of metal to MWCNTs influence electronic transport before and after interconnection.

Key words laser technique; femtosecond laser; multi-wall carbon nanotubes; metal electrode; heterogeneous connection; electrical property

OCIS codes 320.2250; 160.0160; 240.6700