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扫描方向对金属和硅复合薄膜表面激光诱导自组织加工质量的影响(特邀)

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摘　要:激光诱导周期性表面结构的质量可通过调整激光参数、改善材料表面和优化扫描策略等手段来提高。研究了扫描方向对线偏振激光诱导金属/硅复合薄膜表面氧化LIPSS的影响。结果表明,当扫描方向垂直于激光偏振方向时,纳米结构会出现分叉、不连续等问题;当扫描方向平行于激光偏振方向时,纳米结构呈现短程有序,但在光斑拼接处存在扭曲;而当扫描方向与激光偏振方向存在一定夹角时,容易获得长程均匀有序的周期性纳米结构。数值仿真结果表明造成这些现象的原因是近场效应对自组织过程具有不可忽略的影响。

关键词:激光诱导周期性表面结构;表面等离激元;激光诱导化学反应;复合薄膜
中图分类号:V261.8;O644.1　　**文献标识码**:A　　**doi**:10.3788/gzxb20235207.0752303

0　引言

激光诱导周期表面结构(Laser-Induced Periodic Surface Structures,LIPSS)是激光照射在固体表面形成的一种周期性微纳结构[1-2],它的形成和应用是一个跨学科的研究领域,需要涉及到材料科学、物理学、化学、工程学等多个学科的知识,因此促进了这些学科之间的交叉与融合[3-5]。LIPSS作为一种新型的激光表面微纳加工技术[6-8],可以在不使用昂贵设备和化学试剂的情况下,实现大面积、均匀、有序的一维和两维纳米结构制备,对于推动材料科学和微纳技术的发展具有重要意义。

提高大面积LIPSS的质量是当前该领域一个重要的研究方向[9-21]——尽管LIPSS具有加工速度快、鲁棒性高等独特优势,但在实际应用中,其加工质量还存在一些问题,需要采取一些措施来优化制备条件。例如,可以通过调整激光参数、优化扫描策略、改善材料表面处理等手段来控制LIPSS的形态和质量。

近年来,人们发现了扫描方向对大尺寸LIPSS质量的影响,其中比较有代表性的是De La CRUZ A R等报道了利用高重复频率的飞秒激光烧蚀金属铬(Cr)材料,并通过“之”字形扫描得到高质量、大面积周期性结构的实验结果[22]。他们发现,当激光扫描方向垂直于激光偏振时(即垂直于表面等离激元传输方向),得到的周期性纳米结构质量明显优于当激光扫描方向平行于激光偏振方向(即平行于表面等离激元传输方向)时得到的。其原因是对于前者而言,已形成的周期性结构激发的长程表面等离激元对于后续的结构形成具有远场引导作用。

类似地,ÖKTEM B等利用飞秒激光诱导金属钛(Ti)、钨(W)形成氧化LIPSS[13],DOSTOVALOV A等在硅膜上研究氧化LIPSS时也发现了类似的规律[14]。氧化LIPSS是由散射波与入射光干涉导致的,其周期性结构取向平行于激光偏振方向。因此,在这种情况下,当激光扫描方向平行于激光偏振时(即垂直于散射

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波传输方向),更容易得到均匀有序的周期性纳米结构。

从上述两个例子可以看出,当LIPSS由远场干涉主导时,扫描方向需与表面电磁波的传播方向垂直。然而,除了远场干涉,近场效应也可能影响LIPSS的加工质量。南方科技大学的HUANG J等最近对LIPSS不均匀性的电磁起源进行了深入研究[23-24],他们发现了半周期不匹配光近场增强(h-MOE)效应导致的条纹扭曲。h-MOE效应源自于位于每两个相邻波纹之间的近场增强与现有波纹之间存在半周期的不匹配。

本文基于金属/硅复合薄膜体系进一步研究了近场效应对LIPSS均匀性的影响。将高折射率的硅覆盖在金属表面可有效降低等离激元的传输距离,从而有利于分析近场效应的作用。实验发现,当激光扫描方向垂直于表面电磁波传播方向时,LIPSS结构呈现不规则、不连续、整体歪歪扭扭的现象;而当激光扫描方向平行于表面电磁波传播方向时,局部LIPSS质量较高,但在连续扫描时,其拼接质量较差。更重要的是,进一步发现,当扫描方向和偏振方向呈一定夹角时,LIPSS呈现出长程有序、无拼接问题的高质量一维纳米光栅结构。

1 实验与设备

研究采用实验方案如图1所示。使用一个重复频率为5 kHz的二极管泵浦超快光纤放大系统(Amplitude),其中心波长为1 030 nm,脉冲宽度为130 fs。激光束经由一个双色镜耦合到一台光学显微镜中。低倍率物镜(数值孔径NA=0.15)用于将飞秒激光聚焦到安装在3D移动平台上的样品上,而长工作距离物镜(NA=0.85)则方便随时观察激光诱导的表面纳米结构。研究中,选用由100 nm厚金属和50 nm厚非晶硅组成的复合薄膜作为样品。该复合薄膜是通过磁控溅射系统(ULVAC CS200Z)在室温下沉积在玻

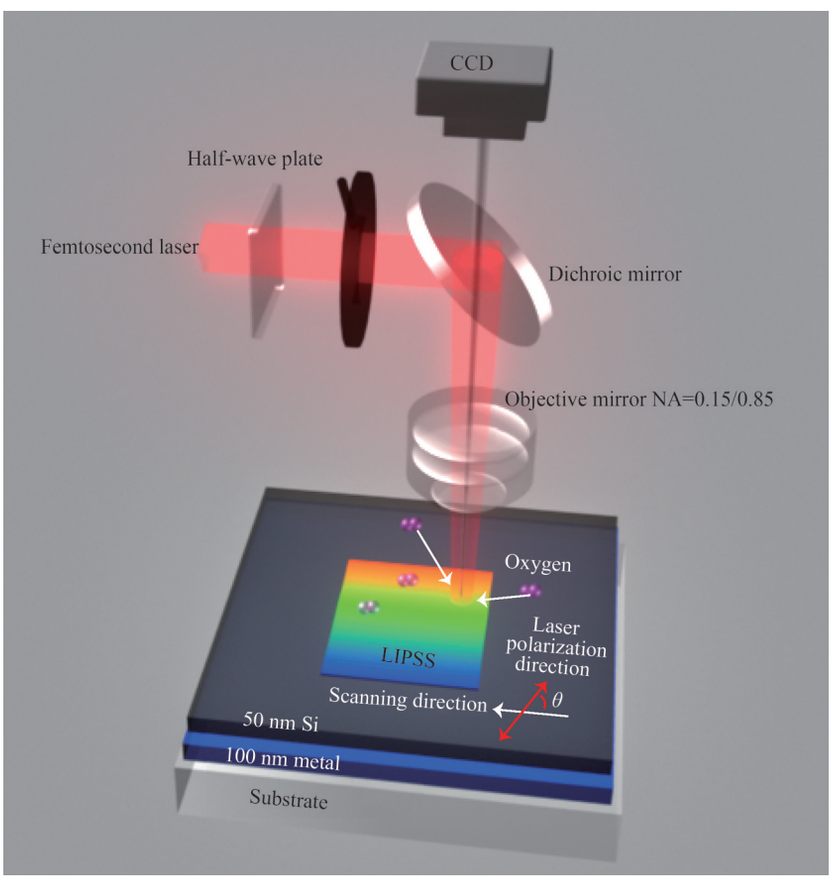


图1 在金属/硅复合薄膜表面利用单束飞秒激光在硅膜上诱导产生氧化LIPSS的原理示意图,位移台扫描方向和激光偏振方向的夹角为θ,激光偏振方向通过半波片调节

Fig. 1 Scheme of oxidative LIPSS formation on metal/Si hybrid films by femtosecond laser irradiation. The crossing angle between the scanning direction and laser polarization direction is defined as θ, the incident laser polarization is controlled by a half-wave plate

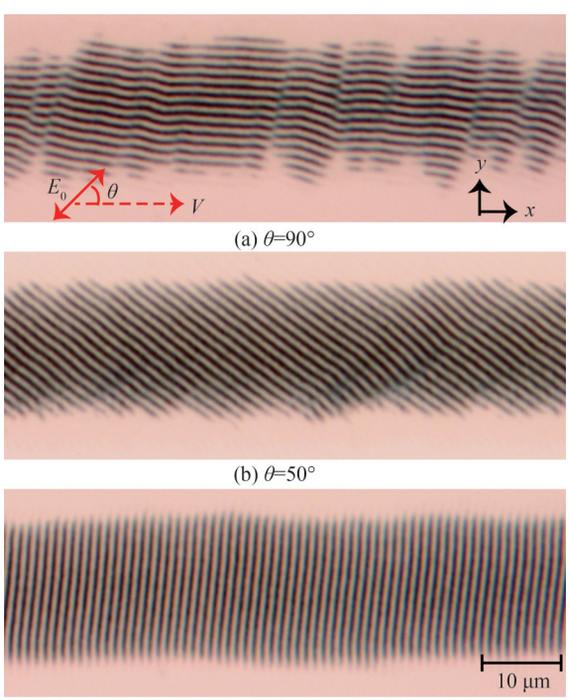
璃基板上的。金属薄膜是在功率为100 W，压力为0.3 Pa，氩气流量为150 sccm的条件下通过直流溅射沉积的，而硅薄膜则是在功率为300 W，压力为0.3 Pa，氩气流量为70 sccm的条件下通过射频溅射沉积在金属薄膜上的。薄膜材料的厚度和介电常数分别由轮廓仪和椭偏仪测量得到。

焦点处激光的能量密度仅约10 mJ/cm^2，远低于硅材料的多脉冲烧蚀阈值（~200 mJ/cm^2）[25]。因此，获得的LIPSS是基于激光诱导氧化反应而非当前广泛研究的烧蚀效应形成的。需要指出的是，氧化LIPSS是近年来才引起人们关注的一种新型的自组织现象[13]，它可以有效地提高加工质量。其原因是多方面的：首先，氧化过程使用的能量非常低，导致产生的热量残余远远低于烧蚀效应；其次，氧化反应是把氧分子注入到材料中形成堆积的氧化物纳米颗粒，不会有大量的烧蚀碎屑喷出——这同时解决了烧蚀LIPSS广泛存在的热量残余和烧蚀碎屑等问题。此外，氧化LIPSS过程中存在一个非线性反馈效应：表面波的强度随氧化物纳米颗粒的直径增大而增强[13,21]。但在以往的研究中，人们主要是在Ti、Cr、W、Si等金属或半导体单层薄膜上加工氧化LIPSS。本文使用金属加半导体复合薄膜具有以下几方面的优点：首先，金属和半导体组成一个共振吸收器，将能量束缚在硅膜中，从而有效提高能量利用效率；其次，相对于单层硅膜表面的短程电磁波，低损耗的金属膜能支持长程表面等离激元的传输，因此可有效增加作用的脉冲数从而提高加工速度。

2 实验结果与分析

图2给出了三种不同扫描方向下，样品沿x方向扫描得到的硅膜表面一维LIPSS结果，其中下层金属材料为铂（Pt）。样品扫描速度为v=5 μm/s，激光重复频率为5 kHz，焦点处能量密度约为10 mJ/cm^2。当扫描方向垂直于激光偏振方向时，如图2（a），θ=90°，即沿着LIPSS取向方向扫描，得到的周期性纳米结构呈现扭曲、不连续等问题。然而，当扫描方向与LIPSS取向有一定夹角时（θ<90°），发现激光诱导的周期性纳米结构呈现出更规则的形貌，如图2（b）、（c）所示。需要指出的是，这里仅展示了金属材料为Pt，θ=50°和θ=0°（扫描方向垂直于LIPSS取向）两种情况，但在银（Ag）、金（Au）等其他金属和其他夹角下该结论也成立。在前期的工作中，已经证实该复合薄膜体系在10 mJ/cm^{2}能量密度下得到的是氧化LIPSS[25]，因此在本文中不再赘述。

从图2中可以得出，扫描方向垂直于激光偏振得到的纳米结构有序性较差。为了深入理解该现象背后



(a) θ=90°

(b) θ=50°

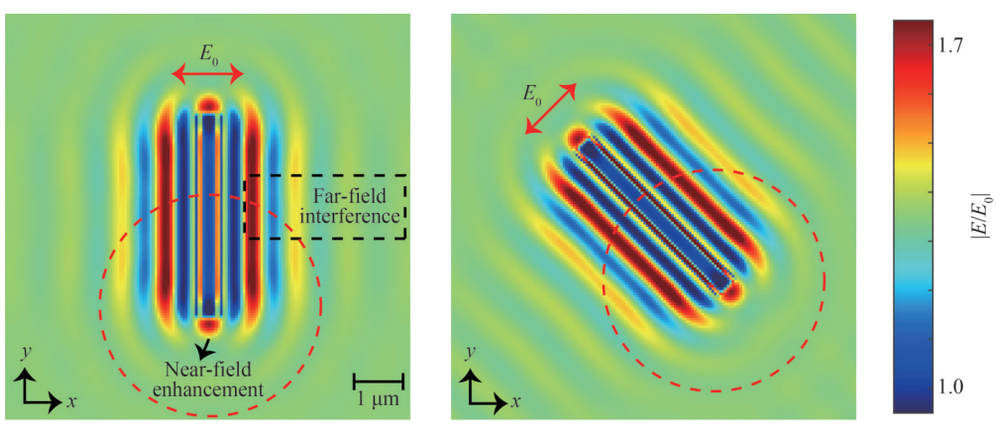
(c) θ=0°

图2 激光偏振方向和扫描方向的夹角不同时，样品沿x方向一维扫描（红色箭头）得到的周期性纳米结构光镜图（V：样品扫描方向；E_0：激光偏振方向）

Fig. 2 Optical microscope images of one-dimensional LIPSS obtained by different crossing angles between scanning direction and laser polarization, the scanning direction is along x-axis (V: sample scanning direction; E_0: laser polarization direction)

的原因，进一步使用数值方法（Lumerical FDTD solutions）对硅膜表面的电场分布进行分析，结果如图3所示。在该仿真中，在硅膜中嵌入一根二氧化硅纳米棒作为散射源，它在激光扫描过程中作为种子结构以诱导逐渐生成周期性结构。为了更契合实验结果，仿真中氧化硅纳米棒的宽度和高度分别是400 nm和100 nm（一半嵌入硅中，一半暴露在空气中）。更多关于数值仿真参数请参考文献[25]。

从图3(a)中可以看出，在纳米棒上下两端（垂直于电场方向）存在较大的近场增强，而在纳米棒左右两侧则具有周期性的远场干涉条纹。因此，当扫描方向沿着纳米棒取向时（y轴），纳米结构的生成将在很大程度上受纳米棒尖端的近场增强影响。如上所述，实验中的氧化LIPSS是由大小不一的氧化物纳米颗粒堆积而成的，因此随扫描过程形成的纳米棒很容易受尖端处纳米颗粒随机分布的影响，从而导致最终获得的LIPSS产生扭曲、分叉、不连续等现象，如图2(a)所示。相反地，当扫描方向垂直于纳米棒取向（x轴，图3(a)）或存在一定夹角时（图3(b)），LIPSS的形成更多地受纳米棒导致的远场干涉影响。因此在这种情况下，产生的LIPSS具有更规则的形貌，如图2(b)、(c)所示。

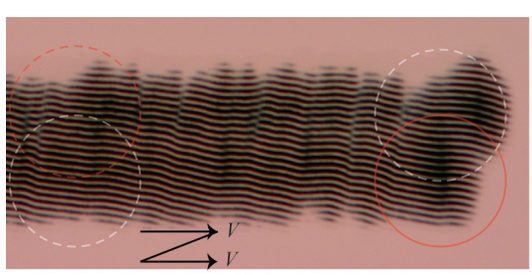


(a) Crossing angle between the silica stripe and x-axis is 90°　(b) Crossing angle between the silica stripe and x-axis is 45°

图3 基于FDTD方法数值模拟在Pt/Si复合薄膜中嵌入二氧化硅纳米棒后的硅膜表面电场分布

Fig. 3 FDTD-based numerical simulation of electric field distribution at Si-air interface when embedding a silica nanostripe into Pt/Si hybrid film

进一步研究不同扫描模式对于多次扫描形成LIPSS的影响，如图4所示。实验中采取的是“之”字形扫描模式，如图4(a)，红色虚线圆圈和实线圆圈分别表示激光光斑的初始位置和最终位置。当扫描方向沿着LIPSS取向时，纳米结构仍然呈现扭曲和不连续等问题。值得注意的是，当扫描方向垂直于LIPSS取向时，虽然单次扫描得到的结构较为整齐，如图2(c)，但在两次扫描的情况下，上下两行光斑拼接处，如图4(b)中黑色方框区域，存在拼接扭曲的问题。然而，当扫描方向与LIPSS取向存在一定夹角时，光斑拼接处的扭曲问题得到了很好的解决，如图4(c)所示。为了进一步理解该现象背后的机理，重新回顾图3中的数值仿真结果。从图3(b)中发现，当扫描光斑照射至倾斜的纳米棒时，纳米棒激发的表面等离激元会传输到尚未形成LIPSS的区域（光斑的下半部分）。这意味着入射激光和表面等离激元的远场干涉会影响后续的LIPSS形成过程。相反地，当扫描方向垂直于纳米棒取向时，表面等离激元只能局限在已形成LIPSS的区域，对后续LIPSS的形成难以产生引导效果，导致光斑上下拼接处由于存在近场耦合而形成扭曲的LIPSS形貌。



(a) θ=90°

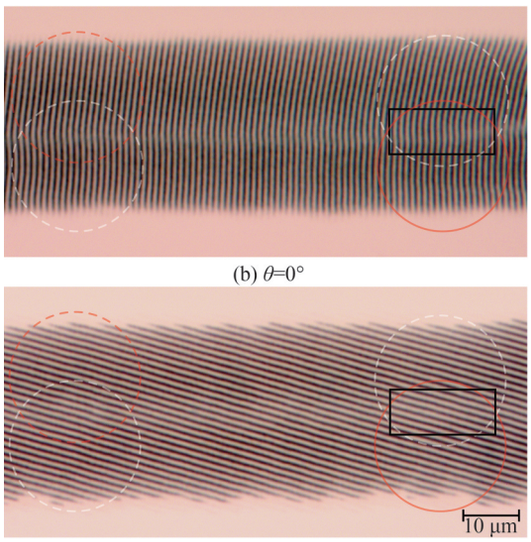


图4　激光偏振方向和扫描方向的夹角不同时，样品沿“之”字形扫描（黑色箭头）得到的周期性纳米结构光镜图（虚线和实线红色圆圈分别表示光斑初始位置和最终位置，上下两行扫描光斑之间的距离为10 μm，黑色方框指示两次扫描的拼接处）

Fig. 4　Optical microscopy images of periodic nanostructures obtained by zigzag scanning (black arrows) in three different crossing angles between scanning direction and laser polarization (The dotted the solid red circles represent the initial and final position of the laser spot, respectively. The distance between the upper and lower scanning spots is 10 μm. The black box indicates splicing area between the adjacent two scans)

3　结论

本文利用LIPSS原理，在金属半导体两层复合薄膜表面，通过单束飞秒激光加工一维周期性纳米结构。研究发现，纳米结构的质量与激光扫描方向密切相关。这是因为自组织过程不仅受到表面电磁波远场干涉的影响，还受到近场增强的影响。因此，最佳的扫描策略不是一般认为的扫描方向垂直于激光偏振方向或平行于偏振方向，而是需要在扫描方向和偏振方向之间选择一个合适的夹角。这不仅可以解决周期性结构经常出现的分叉、不连续等问题，还能有效解决光斑拼接处的扭曲等问题。这项研究可为进一步提高LIPSS加工质量提供新的思路。另一方面，金属薄膜上的周期性电介质/半导体纳米结构在纳米光子学中具有非常广泛的应用，例如：折射率传感[11]、非线性增强[26]、光电探测[27]、结构色等[28-29]，本文研究有望为上述应用提供一种低成本的加工手段。

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Influence of Scanning Direction on the Quality of LIPSS on Metal-Si Hybrid Films (Invited)

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Abstract: Laser-Induced Periodic Surface Structures (LIPSS) have emerged as a powerful tool in nanofabrication and nanophotonics due to their unique optical and surface properties. In recent years, the

long-range uniformity of LIPSS formation have been a subject of extensive research, with efforts focused on optimizing laser parameters, material surfaces, and scanning strategies. In this study, we investigated the influence of scanning direction with respect to laser polarization on the regularity of LIPSS which was produced on metal/silicon hybrid thin films via femtosecond laser-induced surface oxidation.

Our experimental findings revealed intriguing phenomena associated with LIPSS formation under different scanning directions relative to the laser polarization direction. When the scanning direction was perpendicular to the laser polarization, the nanometer-scale structures exhibited irregularities, such as branching and discontinuities. Conversely, when the scanning direction was parallel to the laser polarization, the structures demonstrated short-range order, but undesirable distortion occurred at the overlap of adjacent laser spots. Remarkably, when the scanning direction formed a certain angle with the laser polarization, long-range and uniform periodic nanostructures were readily obtained.

To gain insights into the underlying mechanisms, Finite-Difference Time-Domain (FDTD)-based numerical simulations were conducted to elucidate the role of near-field enhancement and far-field interference during the laser-induced self-organization process. The simulations provided a comprehensive understanding of the interplay between the near-field and far-field effects, showing that near-field enhancements significantly impacted the spatial distribution of LIPSS. Consequently, we proposed an optimal scanning strategy that deviates from the conventional approach of perpendicular or parallel scanning relative to the laser polarization direction. By selecting an appropriate crossing angle between the scanning direction and the polarization direction, we effectively mitigated common issues like branching, discontinuities, and distortion, leading to the generation of high-quality and reproducible periodic nanostructures.

Exploiting our new findings, we successfully fabricated one-dimensional periodic nanostructures on the surface of metal/silicon bilayer films by using single-beam femtosecond laser pulses. The quality and uniformity of the nanostructures were markedly improved by implementing the optimized scanning strategy. This breakthrough not only addresses the challenges associated with LIPSS formation but also opens up exciting opportunities for nanophotonics applications. The potential applications of periodic dielectric/semiconductor nanostructures on metal films in nanophotonics are vast and promising. These structures have demonstrated exceptional capabilities in refractive index sensing, nonlinear optical effects, photodetection, and structural coloring. Moreover, the low-cost and scalable nature of the proposed fabrication method offers great potential for widespread adoption in diverse applications.

In conclusion, this research underscores the significance of optimizing scanning strategies for achieving high-quality and large-scale LIPSS. By considering the interplay of near-field and far-field effects during the self-organization process, we have demonstrated a novel approach to enhance the quality of LIPSS fabrication. Additionally, the applications of periodic nanostructures on metal films in nanophotonics hold promise for revolutionary advancements in various optical devices and technologies. The findings from this study lay the foundation for further exploration of LIPSS-based nanofabrication techniques, paving the way for a new era in nanophotonics and nanotechnology. Through continued research and innovation, LIPSS is poised to play a pivotal role in shaping the future of advanced nanophotonics and nanofabrication, impacting a wide range of scientific and technological domains.

Key words: Laser-Induced Periodic Surface Structures (LIPSS); Surface plasmons; Laser-induced oxidation; Hybrid thin films

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