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两步退火法对硫化铅薄膜光电性能的影响

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摘要 采用先低温O_2气氛退火，后高温N_2气氛退火的两步退火法工艺，探究了两步退火法对化学浴沉积(CBD)制备的多晶硫化铅(PbS)薄膜光电性能的影响。结果表明，相比于一步退火法，两步退火法所得的PbS薄膜具有较大的晶粒尺寸、较少的晶界和良好的光电性能。在两步退火法中，当第二步退火时间为80 min时，PbS薄膜的响应度为2.33 A·W^{-1}，比探测率为1.18×10^{10} cm·H$^{1/2}$·W^{-1}，与一步退火法相比分别提高了259%和236%，即两步退火法可以在传统一步退火法的基础上进一步提高PbS红外光电探测器的性能。

关键词 薄膜；硫化铅薄膜；退火；化学浴沉积；响应度；比探测率

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1 引 言

光电探测器能够将红外辐照信号转化为电信号，在成像、安全、遥感和空间探测等领域中有着广泛的应用[1-7]。近年来，随着红外技术的高速发展，越来越多的半导体材料被引入制作红外光电探测器。硫化铅(PbS)是最早用作红外光电探测器的半导体材料之一[8]，凭借其制备成本低、非制冷、探测率高和响应速度快等优点，目前仍是1~3 μm红外光电探测器的关键材料[9]。

制备PbS薄膜的方法有很多，如化学浴沉积(CBD)、磁控溅射、真空热蒸发和原子层沉积等[10-13]。然而，无论采用何种方法制备的原生PbS薄膜光电性能都很差，只有经过敏化处理之后的PbS薄膜才可用于制作高性能的红外光电探测器[14-15]。研究表明，PbS薄膜中的氧含量会严重影响其光敏性能[14]，并且在含O_2气氛中退火是提高PbS薄膜光电性能的关键。目前，学者们针对PbS薄膜的退火温度、气氛和升温速率等因素对光电性能的影响进行了大量的研究。Preetha等[16]研究了不同退火温度对PbS薄膜光学性能的影响，发现退火温度能显著影响PbS薄膜的光学带隙。Liu等[14]研究了PbS薄膜在不同氮氧比气氛下的退火过程，结果表明在退火过程中N_2不仅可以有效抑制PbS薄膜表面缺陷的产生，还能防止PbS薄膜过度氧化，进而提升了光电性能。Jin等[17]利用快速退火技术在空气气氛中对PbS量子点进行退火，并制作了高性能的PbS量子点红外探测器。以上研究都是在退火装置中一步完成，也就是所谓的一步退火法。一步退火法虽然能够显著提升原生PbS薄膜的光电性能，但是在较高退火温度下容易发生过敏化，无法满足制备高性能PbS红外探测器的需求。如何进一步提高PbS红外探测器的性能依旧困扰着学术界和产业界。

本文采用CBD法制备了PbS薄膜，并提出了一种两步退火法的新工艺，即PbS薄膜先在较低温度的纯O_2气氛中退火，再在更高温度的纯N_2气氛中进行第二步退火。研究了两步法中第二步退火时间对PbS薄膜微观形貌、晶体结构、薄膜厚度和光电性能的影响。结果表明，与一步退火法相比，两步退火法能有效提高PbS薄膜的光电性能。

2 实 验

2.1 PbS薄膜及器件的制备

采用CBD法在玻璃衬底上制备了PbS薄膜。在沉积开始前，先用清洗剂清洗直径为2 inch(1 inch=2.54 cm)的玻璃衬底，再分别在去离子水和无水乙醇中超声清洗10 min，最后烘干。PbS薄膜沉积溶液的总体积为500 mL，由乙酸铅[Pb(CH$_3$COO)$_2$·3H$_2$O，浓度为0.1 mol/L]、柠檬酸三钠($C_6H_5Na_3O_7$，浓度为0.2 mol/L)、氢氧化钾(KOH，浓度为7 mol/L)和硫脲(CH_4N_2S，浓度为3 mol/L)组成，沉积温度为80 ℃，沉积时间为4 h。在沉积结束后，用去离子水冲洗基片并在空气中干燥。最终可得到表面均匀且呈镜面反射的原生PbS薄膜(命名为S1)。先采用光刻工艺在原生PbS薄膜表面形成图形，再将其置于铁氰化钾

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{$K_3[Fe(CN)_6]$}和硫代硫酸钠($Na_2S_2O_3\cdot5H_2O$)质量比为1∶1的溶液中刻蚀10 min,最后去除光刻胶。将处理后的原生PbS薄膜置于纯O_2气氛的管式炉中,以20 ℃/min的速度升温至550 ℃并保温1 h(命名为S2),再使其快速降至室温。将第一步O_2退火后的薄膜置于纯N_2气氛的管式炉中,以20 ℃/min的速度升温至600 ℃进行第二步退火处理,保温10、50、80、110 min(分别命名为S3、S4、S5、S6),再使其快速降至室温。采用光刻和磁控溅射工艺在薄膜表面制作Cr/Au(50 nm/200 nm)电极。电极间距为1 mm,宽度为200 μm(有效面积为1 mm×1 mm)。

2.2 PbS薄膜的表征

采用X射线衍射仪(XRD, RigakuUltima IV)和Cu Kα(λ=0.15406 nm)对样品的物相和晶体结构进行表征。采用光学显微镜(SDPTOP RX50M)观察样品的表面形貌。使用场发射扫描电子显微镜(FESEM, FEI Nova Nano 450)观察样品的表面微观形貌和晶粒尺寸。利用探针式表面台阶仪(Veeco, Dektak150)对薄膜的厚度进行测量。采用实验室自己搭建的光电测试系统对薄膜的光电性能进行表征。该系统在室温下用Keithley 2450数字源表与探针台连接,以波长为1550 nm且功率可调的激光器作为入射光源,用波形发生器控制激光光源的开关。

3 结果与讨论

3.1 晶体结构分析

图1为原生和退火后的PbS薄膜的XRD图谱。样品S1的XRD图谱显示出立方PbS相的衍射峰(JCPDS No. 05-0592),无其他明显的杂峰,表明其为纯相PbS薄膜。所有样品的择优取向均为PbS(200)晶面。在样品S2的XRD图谱中,立方PbS相仍然占据主导地位,同时观察到几个新的衍射峰,说明有新的相生成,通过比对标准PDF卡片,新相的成分为$PbO\cdot PbSO_4$(JCPDS No. 72-1393)。样品S3~S6的XRD图谱特征衍射峰与样品S2相同,没有出现新的衍射峰,说明PbS薄膜在N_2气氛中退火不会生成其他新相。然而,观察到PbS(200)晶面的衍射角(2θ)发生了偏移,这与高温下的热应力有关[18]。

3.2 形貌分析

图2为原生和退火后PbS薄膜的光学显微镜形貌图。由图2(a)可以看出,样品S1的表面形貌平整且均匀。在图2(b)中,样品S2表面出现了大量的圆形凸起结构,这是由O_2退火后生成新的氧化相导致的。从图2(c)~(f)可以观察到,随着第二步退火时间的延长,样品S4~S6的表面开始出现孔洞。其中,样品S6的表面孔洞最多,这可能会对PbS薄膜的光电性能产生不利影响。Kamchatka等[20]的研究表明,PbS在温度高于577 ℃下退火时会发生严重的升华。对于样品S4~S6,第二次退火的温度为600 ℃,故孔洞的出现与高温下的升华有关。

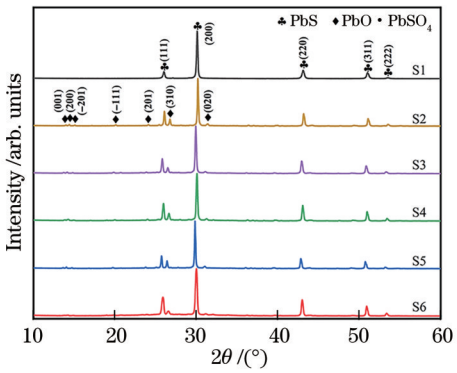

图1　样品S1~S6的XRD图谱

Fig. 1　XRD patterns of samples S1-S6

图3为原生和退火后PbS薄膜的扫描电子显微镜(SEM)形貌图。从图3(a)可以观察到,样品S1由粒径为100~600 nm的PbS立方晶粒组成,表面形貌均匀且致密。样品S2的表面形貌如图3(b)所示,经过550 ℃的纯O_2气氛退火后,薄膜的表面由原始的立方晶粒变为均匀分布的鹅卵石状晶粒,平均晶粒尺寸约为235 nm,晶粒尺寸的减小是由薄膜的氧化引起的[20]。结合样品S2的XRD图谱中出现的$PbO\cdot PbSO_4$特征峰,经过550 ℃的纯O_2气氛退火后形成的鹅卵石状晶粒可能是由$PbO\cdot PbSO_4$相包裹的PbS晶粒所组成的。从图3(c)~(f)可以观察到,与样品S2相比,第二步600 ℃纯N_2退火后的样品(样品S3~S6)表面的鹅卵石状晶粒尺寸增大(约为350 nm),这是因为鹅卵石状晶粒在高温热力学驱动力的作用下晶粒会发生再结晶[21-22]。此外,在退火后的薄膜表面都观察到了裂纹,这是由退火后的快速降温过程中PbS薄膜与玻璃衬底的热膨胀系数(玻璃和PbS的热膨胀系数分别为$8.9\times10^{-6}\ K^{-1}$和$20.3\times10^{-6}\ K^{-1}$[23])失配所引起的。

3.3 光电性能和厚度分析

图4为光电性能测试示意图和不同光功率密度下PbS薄膜的光电性能,此时偏置电压为50 V。图4(a)为PbS光电探测器的测试示意图。图4(b)显示了PbS光电探测器的光生电流(I_{ph})与入射激光功率密度(P)之间的关系,其中I_{ph}是光电流(I_{light})与暗电流(I_{dark})之差($I_{ph}=I_{light}-I_{dark}$)。从图4(b)可以观察到,随着$P$值的增加,样品S2~S6的$I_{ph}$值非线性增加,且逐渐趋向于饱和。在相同的$P$值下:随着两步法中第二步退火时间的增加(从10 min到80 min),样品S2~S5的I_{ph}值呈逐渐增大的趋势;当退火时间为110 min时,样品S6的I_{ph}值显著下降,且在较高的入射激光功率密度下这种下降更为明显。当P=12.7 mW·mm^{-2}时,样品S2~S6的I_{ph}值分别为2.12、2.12、2.20、1.03 mA。图4(c)和图4(d)分别为样品的响应率$R[R=I_{ph}/(PA)]$和比探测率$D^*(D^*=R\sqrt{A}/\sqrt{2qI_{dark}})$随$P$值变化的曲

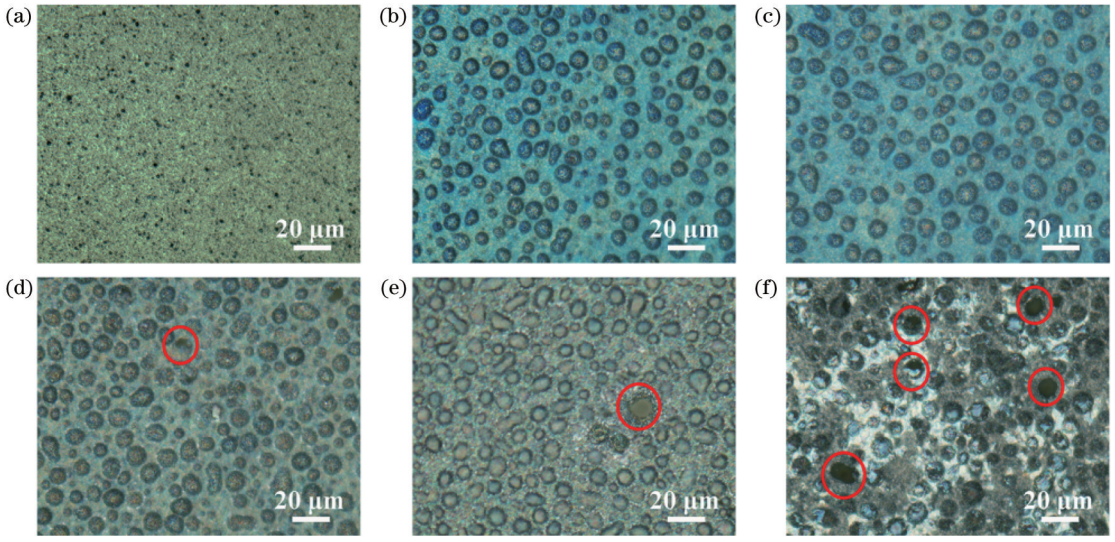

图 2　样品 S1～S6 的光学显微镜表面形貌图。(a)样品 S1;(b)样品 S2;(c)样品 S3;(d)样品 S4;(e)样品 S5;(f)样品 S6

Fig. 2　Optical microscope surface morphologies of samples S1-S6. (a) Sample S1; (b) sample S2; (c) sample S3; (d) sample S4; (e) sample S5; (f) sample S6

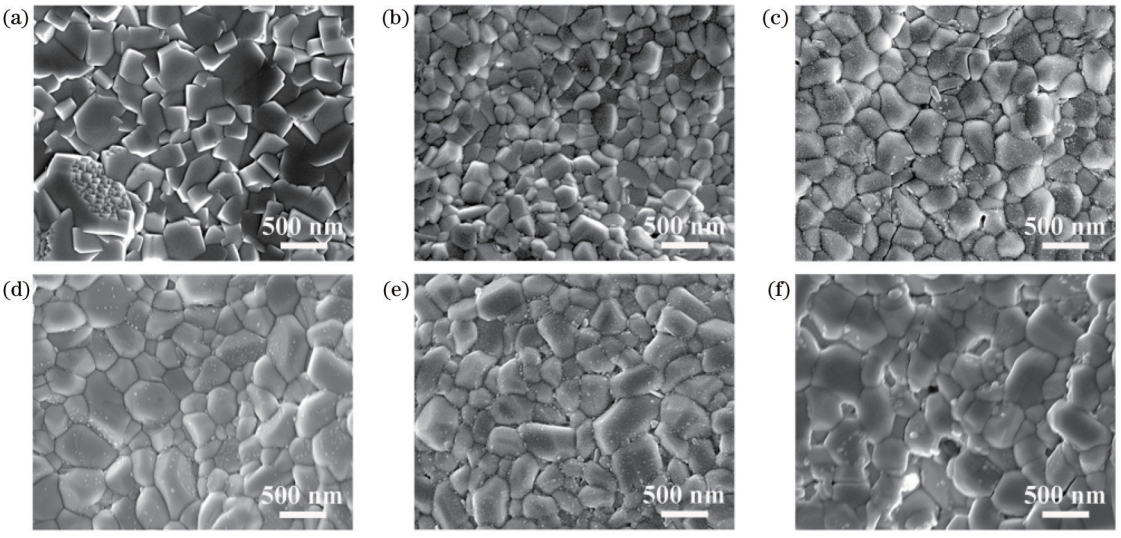

图 3　样品 S1～S6 的 SEM 表面形貌图。(a)样品 S1;(b)样品 S2;(c)样品 S3;(d)样品 S4;(e)样品 S5;(f)样品 S6

Fig. 3　SEM surface morphologies of samples S1-S6. (a) Sample S1; (b) sample S2; (c) sample S3; (d) sample S4; (e) sample S5; (f) sample S6

线,其中 A 为有效面积($A=1\ \text{mm}\times 1\ \text{mm}$),$q$ 为基本电荷($q=1.6\times 10^{-19}\ \text{C}$)。从图 4(c)、(d)中可以观察到:样品 S2～S6 的 R 值和 D^* 值都随着 P 值的增加而减小,且在较小的入射激光功率密度下更为明显;随着 P 值继续增大,R 值和 D^* 值的下降趋势逐渐趋向平缓。这种现象是由随着入射激光功率密度的增大,虽然光生载流子的数量增加,但是光子转化为 I_{ph} 的效率降低所导致的。可以发现,当 P 值较小时,可以获得更高的 R 值和 D^* 值,这与 Liu 等[10]报道的结果相同。

图 5(a)为所有 PbS 薄膜样品的厚度结果图,样品 S1～S6 的厚度分别为 1031、1894、1634、1573、1176、796 nm。与样品 S1 相比样品 S2 的厚度显著增加,这是因为在第一步退火过程中,PbS 薄膜与 O_2 反应生成了新的氧化相,体积发生了膨胀[20]。随着第二步退火时间的增加,样品 S3～S6 的厚度呈现逐渐减小的趋势,且与其他样品相比,样品 S6 的厚度降低最为显著。这是因为两步法中第二步退火是在 N_2 气氛中进行的,并没有生成新的氧化相,但第二步退火的温度较高会导致薄膜升华,进而引起薄膜厚度降低。样品 S2～S6 的 I_{dark} 值和 R 值(测试偏压为 50 V,光功率密度为 $0.2\ \text{mW}\cdot\text{mm}^{-2}$,入射光波长为 1550 nm)如图 5(b)和图 5(c)所示。可以观察到,样品 S3 的 I_{dark} 值和 R 值较样品 S2 都有增加,是因为两步退火法中第二步退火温度较第一步退火温度有所升高,通过图 3 的 SEM 形貌图可以观察到,第二步退火使晶粒发生再结晶,引起晶粒长大,晶界减少[22]。通过第二步高温 N_2 退火使晶粒

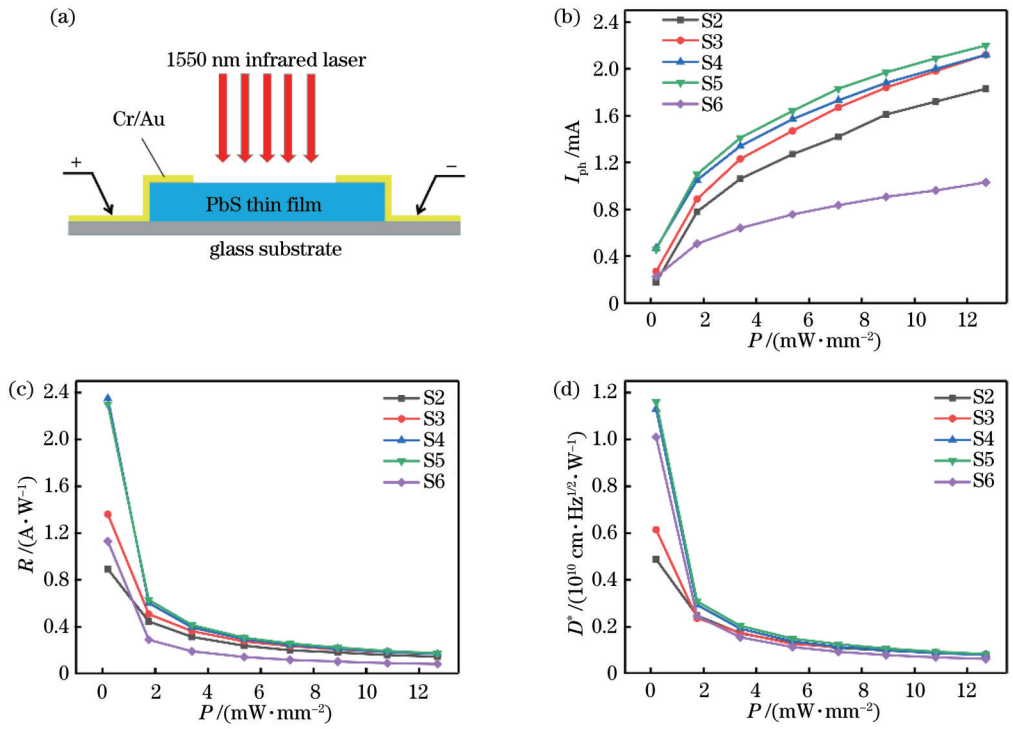

图 4　光电性能测试示意图和不同光功率密度下 PbS 薄膜的光电性能。(a)光电性能测试示意图；(b)I_{ph}；(c)R；(d)D^*

Fig. 4　Schematic diagram of optoelectronic property test and optoelectronic properties of PbS thin films at different optical power densities. (a) Schematic diagram of optoelectronic property test; (b) I_{ph}; (c) R; (d) D^*

发生再结晶提高了晶体质量，产生更多的光生载流子，同时晶界减少还降低了载流子输运所需要克服的势垒。随着两步退火法中第二步退火时间的增加，晶体的质量进一步提高，样品 S4 的 R 值增加。然而，长时间的高温热处理在提高晶体质量的同时也伴随着薄膜的升华(使得薄膜厚度降低)，并且衬底与 PbS 薄膜之间的热膨胀系数失配会使得 PbS 薄膜产生裂纹，导致样品 S4 的 I_{dark} 值减小。随着两步退火法中第二步退火时间的进一步增加，升华变得更加严重，样品 S5 的 I_{dark} 值和 R 值都出现了降低趋势。当两步退火法中第二步退火时间为 110 min 时，样品 S6 的 I_{dark} 值和 R 值都出现了明显的下降，厚度也达到了最低。此时，从图 2(f)可以观察到，样品 S6 表面出现了较多孔洞，部分晶粒之间的连接被断开，这种现象会导致载流子的产生和输运效率都显著降低。由此可见，两步退火法中第二步长时间高温退火会显著影响 PbS 薄膜的 I_{dark} 值和 R 值，降低薄膜光电性能。样品 S2～S6 的 D^* 值(测试偏压为 50 V，光功率密度为 0.2 mW·mm^{-2}，入射光波长为 1550 nm)如图 5(d)所示。可以观察到，随着两步退火法中第二步退火时间的增加，样品的 D^* 值呈现先增大后减小的趋势。当第二步退火时间为 80 min 时，样品 S5 的 D^* 值达到最大值，与一步退火法的样品 S2 相比，提高了 236%(从 5×10^9 cm·Hz$^{1/2}$·W^{-1} 增加至 1.18×10^{10} cm·Hz$^{1/2}$·W^{-1})，R 值也提高了 259%(从 0.90 A·W^{-1} 到 2.33 A·W^{-1})。

在两步退火法的第一步退火过程中，O_2 不仅与 PbS 薄膜表面晶粒发生反应生成 PbO·PbSO$_4$ 相，还会沿着 PbS 晶界扩散到薄膜内部。然而，生成的氧化相不足以完全阻断载流子在 PbS 薄膜内部的输运。在两步退火法的第二步退火过程中，高温 N_2 退火使 PbS 晶体质量提高的同时也伴随着严重的升华。由此可见，合理控制第二步退火时间既可以提高 PbS 薄膜的晶体质量，又可以避免 PbS 薄膜发生严重的升华。最终可使 PbS 红外光电探测器得到相对较高的 R 值和较低的 I_{dark} 值，获得较高的 D^* 值。

为了研究 PbS 薄膜的高频率响应特性，测试样品 S5 在 4 kHz 高频脉冲光照下的响应，此时偏置电压为 50 V，P 值为 0.2 mW·mm^{-2}，入射波长为 1550 nm。样品 S5 的 I_{ph}-t 归一化曲线如图 6 所示，其中 t 为时间。可以发现，样品 S5 具有良好的高频稳定性。结果表明，两步退火法处理后的样品可以实现高频稳定响应。

4　结　　论

采用 CBD 法合成制备了多晶 PbS 薄膜，研究了两步退火法对 PbS 薄膜光电性能的影响。首先，在 550 ℃温度的纯 O_2 气氛下对 PbS 薄膜进行第一步退火。然后，将 O_2 退火后的薄膜在 600 ℃的 N_2 气氛下进行第二步退火。系统地研究了第二步退火时间对 PbS 薄膜光电性能的影响。研究表明，当第二步退火时间为 80 min 时，在偏压为 50 V、光功率密度为 0.2 mW·mm^{-2} 和入射波长为 1550 nm 的测试条件下，样品的 R 值达到 2.33 A·W^{-1}，D^* 值达到

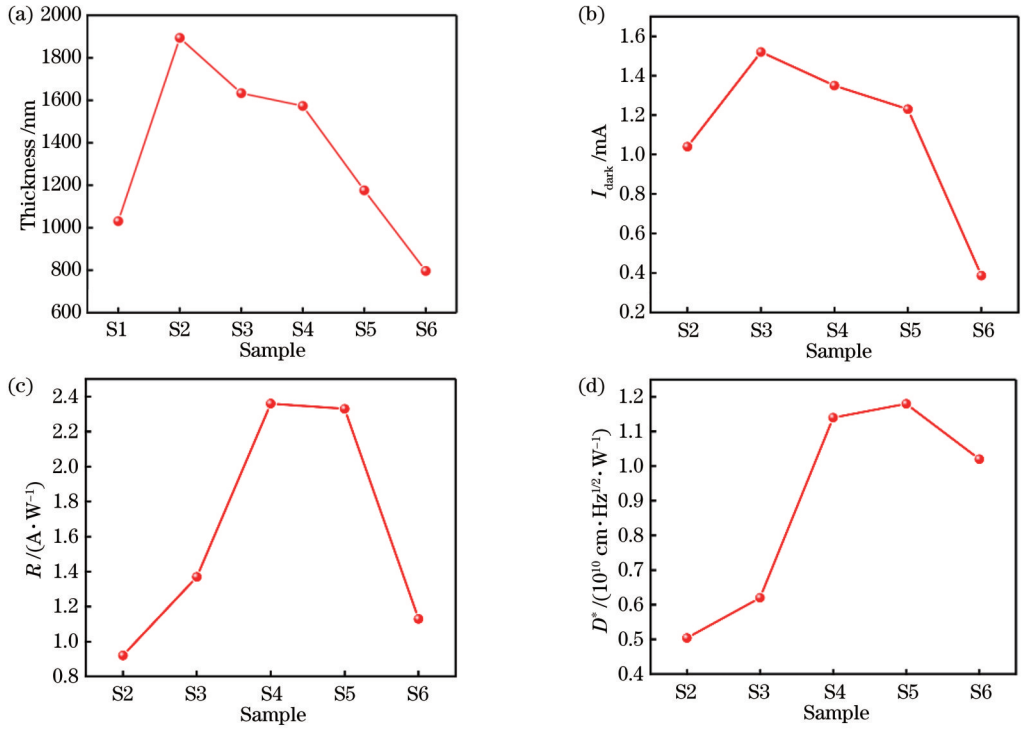

图 5 PbS 薄膜的厚度与光电性能。(a)样品 S1～S6 的厚度;(b)样品 S2～S6 的 I_{dark};(c)样品 S2～S6 的 R;(d)样品 S2～S6 的 D^*

Fig. 5 Thicknesses and optoelectronic properties of PbS thin films. (a) Thicknesses of samples S1-S6; (b) I_{dark} of samples S2-S6; (c) R of samples S2-S6; (d) D^* of samples S2-S6

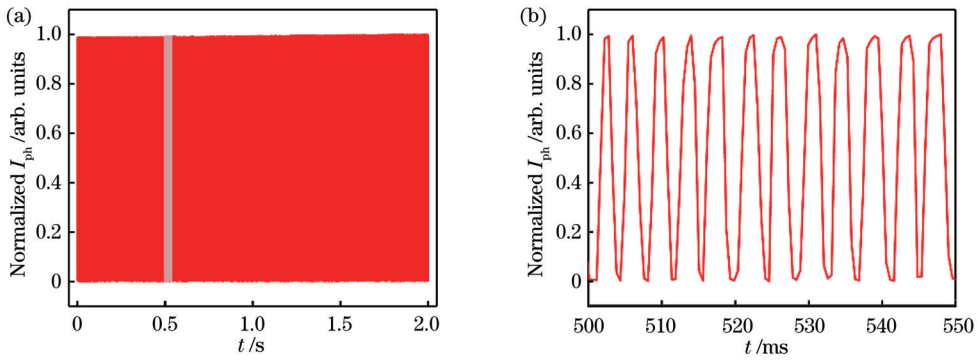

图 6 样品 S5 的高频响应图。(a) 4 kHz 下的归一化响应曲线;(b)图 6(a)中的部分放大图

Fig. 6 Response diagram of sample S5 at high frequency. (a) Normalized response curve at 4 kHz; (b) partial magnification of Fig. 6(a)

1.18×10^{10} cm·Hz$^{1/2}$·W^{-1}。与一步退火法的 PbS 薄膜相比,样品的 R 值和 D^* 值分别提高 233% 和 236%。结果表明,两步退火法可以在传统一步退火法的基础上进一步提高 PbS 红外光电探测器的性能。

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Effect of Two-Step Annealing on Optoelectronic Properties of Lead Sulfide Thin Films

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Abstract

Objective Lead sulfide (PbS) is an important semiconductor material in group Ⅳ-Ⅵ semiconductors with a narrow band gap (0.41 eV) and a large exciton Bohr radius (18 nm) at room temperature. These characteristics make PbS highly sensitive to infrared (IR) radiation, which has led to the widespread use of PbS films in IR detectors, solar cells, gas sensors, and other fields. The as-grown PbS thin films respond poorly to IR and can only be used as highly sensitive IR detectors after sensitization. Annealing in oxygen is an effective method to enhance the photosensitivity of PbS detectors, and oxygen has been proven to be the best sensitizer. Although numerous studies have been carried out on one-step annealing in an oxygen-contained atmosphere, the development of new methods to further improve thin films′ responsiveness to IR continues to plague academia and industry. In this work, a new two-step sensitization treatment process for as-grown PbS thin films by the chemical bath deposition (CBD) method is investigated, in which the films are first annealed in oxygen at a low temperature and then re-annealed in nitrogen at a higher temperature. It is shown that this process can effectively improve the optoelectronic properties of PbS thin films compared with pure oxygen annealing.

Methods PbS thin films are fabricated on glass substrates by the CBD method. The reaction solution is composed of lead acetate [$Pb(CH_3COO)_2 \cdot 3H_2O$], trisodium citrate ($C_6H_5Na_3O_7$), potassium hydroxide (KOH), and thiourea (CH_4N_2S). The cleaned glass substrates are immersed in the deposition bath. After deposition, the samples are rinsed with deionized water and dried. The as-grown PbS films are uniform, mirror-reflective films, and subsequently, they are annealed in oxygen for 1 h at 550 ℃. Lastly, the oxygen-annealed thin films are re-annealed in nitrogen at 600 ℃ for 10 min, 50 min, 80 min, and 110 min. The Cr/Au electrodes are realized by the magnetron sputter, and the phase and crystal structure of these samples are characterized by the X-ray diffractometer. The surface morphology of the samples is observed by optical microscope

and scanning electron microscope (SEM), and the thicknesses of the films are measured by the step profiler. The photoelectric properties are evaluated by a photoelectric test system with a source meter connected to a probe station at room temperature. Lasers are used as excitation sources, and a waveform generator is employed to control the switching of the lasers.

Results and Discussions The as-grown PbS thin film shows a dense, compact surface morphology. After oxygen annealing, the new oxidation phase is formed (Fig. 1). Some holes are observed on the surface of the annealed thin films as the re-annealing continues (Fig. 2). The grains of re-annealed thin films recrystallize to form larger nanocrystals powered by the thermodynamic driving force at high temperature (Fig. 3). The study of photoelectric properties shows that the photocurrent of samples increases before it declines with the re-annealing time at different power densities [Fig. 4 (b)]. The responsivity and specific detectivity of thin films drop as the light power density increases [Fig. 4(c) and Fig. 4(d)]. Although the number of photogenerated carriers increases with the rise in light power density, the conversion efficiency of photons into photocurrent is reduced. As the re-annealing time goes by, the values of specific detectivity and responsivity both increase first and then decrease. For a short period of re-annealing, the grains recrystallize to form microcrystals with high crystal quality, which allows the specific detectivity and responsivity values to rise. As the re-annealing time further increases, over re-annealing not only reduces the thicknesses of the films but also creates holes, which leads to lower specific detectivity and responsivity. The optimum value of specific detectivity is obtained at a re-annealing time of 80 min when the specific detectivity and responsivity values are 236% (5×10^{9} cm·Hz$^{1/2}$·W^{-1} to 1.18×10^{10} cm·Hz$^{1/2}$·W^{-1}) and 259% (0.90 A·W^{-1} to 2.33 A·W^{-1}) higher than those of thin films only annealed in oxygen, respectively[Fig. 5 (c) and Fig. 5(d)]. In addition, the sample re-annealed for 80 min exhibits high-frequency switching behavior and excellent stability at 4 kHz (Fig. 6).

Conclusions In this study, polycrystalline PbS thin films are prepared by the CBD method. The thin films are sensitized with the two-step annealing method, in which the thin films are first annealed in oxygen at a low temperature and then re-annealed in nitrogen at a higher temperature. Appropriate nitrogen re-annealing time improves photoelectric properties by improving the crystal quality of thin films. The results show that the photoelectric properties of the PbS thin films sensitized with the two-step annealing method are significantly enhanced. Compared with the case of one-step annealing, the responsivity of thin films annealed in two steps with a re-annealing time of 80 min can be increased to 2.33 A·W^{-1}, an increase of about 259%, and the specific detectivity is raised to 1.18×10^{10} cm·Hz$^{1/2}$·W^{-1}, a growth rate of about 236%, under the light power density of 0.2 mW·mm^{-2} and incident wavelength of 1550 nm. Additionally, the sample re-annealed for 80 min shows high-frequency switching behavior and excellent stability at 4 kHz. More importantly, two-step annealing can improve the photoelectric properties of the photodetectors on the basis of the traditional oxygen-sensitized thin films.

Key words thin films; PbS thin films; annealing; chemical bath deposition; responsivity; specific detectivity