

基于氧化锌涂层无芯光纤的氨气传感器研究

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摘要 为实现大气污染物中氨气(NH_3)的快速、准确测量,本文提出了一种基于氧化锌(ZnO)涂层单模-无芯-单模(SNS)光纤结构的高灵敏度 NH_3 传感器。该传感器利用的是 ZnO 膜层吸附 NH_3 后自身折射率改变,进而导致无芯光纤干涉谱谐振波长发生变化的特性。通过建立 NH_3 体积分数与谐振波长偏移量的关系,最终实现了 NH_3 体积分数的测量。本文基于模式传输理论对 ZnO 涂层 SNS 传感器的光谱特性进行了仿真,仿真结果显示:当 ZnO 膜层的折射率从 1.929 变化至 1.889 时,60 nm 和 130 nm ZnO 膜厚下 SNS 传感器的灵敏度分别为 11.8 nm/RIU 和 28.6 nm/RIU。制备了 ZnO 膜厚分别为 60 nm 和 130 nm 的 SNS 传感器,其在 NH_3 体积分数为 $0\sim 42.0\times 10^{-6}$ 环境下的灵敏度相差不大,这主要是由 ZnO 对 NH_3 的吸附饱和引起的。进一步分析获得 60 nm ZnO 膜厚下 SNS 传感器的平均灵敏度为 16.87×10^6 pm,检测限为 6.6×10^{-6} ,响应时间和恢复时间分别为 70 s 和 90 s。随着温度由 $16.5\text{ }^\circ\text{C}$ 升至 $56\text{ }^\circ\text{C}$,该传感器对 NH_3 的检测灵敏度从 17.96×10^6 pm 降低至 7.57×10^6 pm,温度和时间对检测限的影响分别为 $0.0237\times 10^{-6}\text{ }^\circ\text{C}^{-1}$ 和 $0.026\times 10^{-6}\text{ d}^{-1}$,该传感器具有较好的稳定性。

关键词 传感器; 无芯光纤; 氧化锌; 氨气测量; 温度

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1 引言

氨气(NH_3)是工业生产中常见的有毒有害的刺激性气体^[1],美国劳工部职业安全与健康管理局(OSHA)规定人类在 NH_3 体积分数超过 25×10^{-6} 的环境中工作不能超过 8 h,在 NH_3 体积分数超过 35×10^{-6} 的环境中工作不能超过 15 min^[2-3]。人体摄入过量 NH_3 会导致肺部肿胀,甚至会致人死亡。因此,对 NH_3 进行检测十分重要。

目前已有多种方法被应用于 NH_3 检测^[4],主要包括电化学检测^[5]和光学检测^[6]。电化学检测主要基于化学反应进行 NH_3 检测,其检测限^[7]可低至 0.5×10^{-6} ,但无法实时在线监测。光学检测可以分为吸收光谱型检测^[8]、倏逝波型检测^[9]和折射率变化型检测^[10]。吸收光谱型检测方法通过检测特定波段的吸收谱线来实现气体浓度的检测^[11],对 NH_3 的检测灵敏度^[12]可达到 3.9×10^{-10} ,但该方法易受其他相同吸收波段气体的影响,对低浓度 NH_3 的测量误差偏大。倏逝波型检测方法通过倏逝场的变化来感应气体浓度。张敏等^[13]采用火焰熔融拉锥技术将保偏光纤拉制成光纤锥形传感器,实现了 176.08×10^6 pm 的高灵敏度 NH_3 检测,但该方法对拉锥工艺的要求非常高,不合适的拉锥参数可能会出现传输损耗增大或者高阶模式截止等,进而导

致干涉谱消失^[14]。折射率变化型检测方法的原理为:在光纤表面涂覆特定的敏感膜,敏感膜折射率随外界待测气体浓度的变化而变化,从而引起传输光谱中谐振波长的漂移,由此可以反推计算得到待测气体的浓度^[15]。Hao 等^[16]在两个 3 dB 长周期光纤光栅构成的多模干涉仪上涂覆一层石墨烯制备了 NH_3 传感器,该传感器对 NH_3 检测的灵敏度为 3×10^6 pm。Huang 等^[17]通过层层自组合法在薄芯光纤表面制备出聚丙烯酸/聚丙烯胺盐酸盐复合薄膜,该复合薄膜的多层结构可以有效吸附 NH_3 ;基于该薄膜的传感器对 NH_3 检测的灵敏度达到了 27×10^6 pm,但其制备工艺较为复杂。近年来,以氧化锌(ZnO)作为敏感膜的光纤传感器成为研究热点^[18], ZnO 对 NH_3 具有较强的吸附性能^[19],当 NH_3 吸附在 ZnO 薄膜表面时会引起 ZnO 薄膜的折射率变化^[20]。Zhu 等^[21]将 ZnO 薄膜与锥形多模光纤结合,实现了灵敏度为 1.5×10^6 pm 的 NH_3 检测;Fu 等^[22]进一步将掺杂氧化石墨烯的氧化锌(GO- ZnO)与锥形七芯光纤结合,利用 GO 来提高 ZnO 表面的电子转移率,制作了灵敏度高达 31×10^6 pm 的 NH_3 传感器。无芯光纤是一种没有纤芯的特殊多模光纤,其内部传输模式较多,其模场可以直接感应外界环境变化^[23]。将 ZnO 与无芯光纤结合来实现 NH_3 检测不失为一种良好的传感方案,但目前尚未见相关研究报道。

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本文提出了一种基于 ZnO 涂层的单模-无芯-单模 (SNS) 光纤结构高灵敏度 NH₃ 传感器。理论上, 基于模式传输理论建立了不同 ZnO 膜厚下的 SNS 传感模型, 采用 MATLAB 软件仿真了 ZnO 涂层无芯光纤中的模场分布, 分析了 ZnO 膜层折射率随激发系数、自映像长度的变化规律, 重点研究了不同 ZnO 膜厚下 SNS 传感器灵敏度随 ZnO 膜层折射率的变化。采用扫描电镜对 ZnO 薄膜的厚度及形貌进行了表征, 并分析了不同 ZnO 膜厚下 SNS 传感器对 NH₃ 的检测灵敏度, 重点对 60 nm ZnO 膜厚下 SNS 传感器的检测限、响应恢复时间进行测试分析, 并进一步讨论了温度对 NH₃ 体积分数检测的影响。

2 理论与仿真

2.1 理论分析

在无芯光纤表面涂覆一层 ZnO 薄膜后, 可以将无芯光纤作为纤芯, ZnO 薄膜与空气视为第 1 和第 2 包层。无芯光纤涂覆 ZnO 薄膜后的 SNS 传感结构的三维示意图如图 1(a) 所示, 该传感器由入射单模光纤 1 (SMF1)、无芯光纤和出射单模光纤 2 (SMF2) 组成, 且 3 段光纤共轴。当入射光从 SMF1 进入无芯光纤时, 由于模场直径不匹配, SMF1 和无芯光纤的界面处会激发出一系列高阶模, 模场穿透 ZnO 膜层后在空气中逐渐变为 0。当光会聚至 SMF2 时, 不同的高阶模之间发生干涉^[24]。图 1(b) 为涂覆 ZnO 薄膜的无芯光纤的折射率分布示意图, 其中, n_1 、 n_2 与 n_3 分别为无芯光纤、ZnO 膜层及外界空气层的折射率, a 和 b 分别为纤芯和 ZnO 膜层的半径, h 为 ZnO 膜层的厚度。

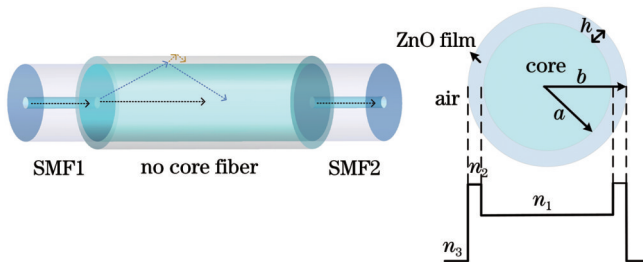


图 1 涂覆 ZnO 后的 SNS 结构。(a) 三维示意图; (b) 无芯光纤的折射率分布图

Fig. 1 Structure of SNS coated with ZnO. (a) Three-dimensional diagram; (b) refractive index profile of no-core fiber

由于无芯光纤是理想的圆对称结构, 在与 SMF 无偏心熔接后, 无芯光纤中只有高阶本征模式 LP_{0m} 被激发^[25]。将 SMF1 输入的光场记为 $E(r, 0)$, 无芯光纤中第 m 阶模场分布记为 $\psi_m(r)$, 根据电磁场的连续性条件, SMF1 与无芯光纤连接处的光场^[26] 可以表示为

$$E(r, 0) = \sum_{m=1}^M c_m \psi_m(r), \quad (1)$$

式中: r 是无芯光纤的半径; M 是无芯光纤中存在的

LP_{0m} 数量; c_m 是第 m 阶高阶模的激发系数, 可以通过 $\psi_m(r)$ 与 $E(r, 0)$ 的重叠积分求得^[27-28], 即

$$c_m = \frac{\int_0^\infty E(r, 0) \psi_m(r) r dr}{\int_0^\infty \psi_m(r) \psi_m(r) r dr}. \quad (2)$$

当光在无芯光纤中传播一定距离 (L) 后, 其传输的场分布^[29] 可以表示为

$$E(r, L) = \sum_{m=1}^M c_m \psi_m(r) \exp(i\beta_m L), \quad (3)$$

式中: β_m 是第 m 阶高阶模的纵向传播常数。当无芯光纤中的光传输至 SMF2 并输出时, 其归一化光透过率^[30] 可以表示为

$$T = 10 \lg \left[\frac{\left| \sum_{m=1}^M c_m^2 \exp(-i\beta_m L) \right|^2}{\sum_{m=1}^M c_m^2} \right]. \quad (4)$$

2.2 仿真分析

本文采用 MATLAB 软件进行编程, 对 ZnO 涂层无芯光纤的模式特性及 ZnO 涂层 SNS 结构的传感特性进行仿真分析。若无特别说明, 仿真中所采用的参数如下: 入射光波长 $\lambda = 1550$ nm; SMF 纤芯折射率 $n_{\text{core}} = 1.4681$, 包层折射率 $n_{\text{clad}} = 1.4629$, 纤芯半径 $r_1 = 4.5$ μm , 包层半径 $r_2 = 62.5$ μm , 无芯光纤半径 $a = 62.5$ μm , 折射率 $n_1 = 1.444$; ZnO 折射率 $n_2 = 1.929$ ^[31]。

图 2 展示了不同 ZnO 膜厚下无芯光纤中 LP₀₁~LP₀₄ 的模场分布。由图 2(a) 可知, 不同 ZnO 膜厚下相同阶的模场分布趋势一致, 模场变化量非常小, 并且各个高阶模的模场分布随无芯光纤半径的增加呈现振荡衰减的趋势。图 2(b) 为不同 ZnO 膜厚下 LP₀₁~LP₀₄ 模场的二维分布图, 各模场均呈圆对称分布。

由式 (4) 可知 SNS 传感器的干涉谱与无芯光纤的模式激发系数、有效传播常数和无芯光纤长度息息相关, 而本文传感器的工作原理实质上是吸附 NH₃ 后引起 ZnO 膜层折射率变化, 进而引起谐振波长漂移, 从而实现 NH₃ 体积分数的检测。NH₃ 的折射率约为 1.000374^[32], 氮气的折射率近似为 1^[33], 因此, 体积分不同的 NH₃ 的折射率变化极小。随着 NH₃ 的体积分数增加, 吸附 NH₃ 后的 ZnO 的折射率变小^[34], 但目前鲜有 ZnO 吸附 NH₃ 后折射率变化的相关报道。本文以下的理论仿真皆是基于 ZnO 吸附 NH₃ 后其折射率从 1.929 变化至 1.889 的假设进行的。

不同 ZnO 膜厚下无芯光纤的模式激发系数如图 3 所示。当膜厚 (h) 一定时, 模式激发系数随模式阶数 m 的增加而先增大后减小, 直至趋于 0。LP₀₄ 的模式激发系数最大, 膜厚为 60 nm 和 130 nm 时 LP₀₄ 的模式激发系数分别为 0.39655 和 0.39626。进一步分析可知模式

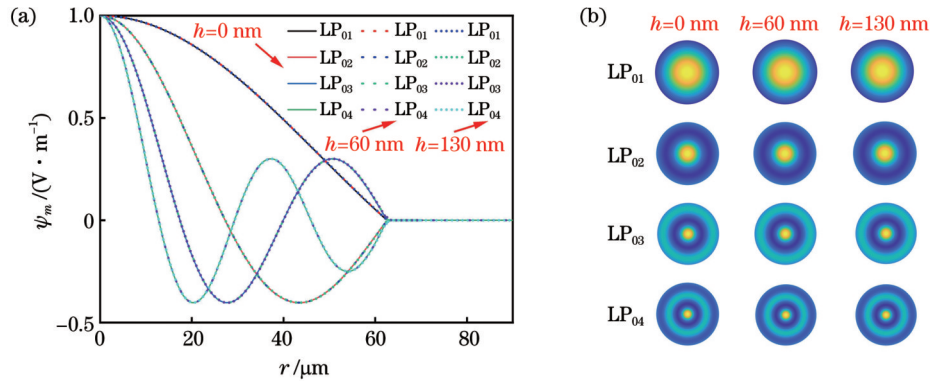


图 2 不同 ZnO 膜厚下无芯光纤的前 4 阶模场分布。(a) 模场随无芯光纤半径的变化; (b) 模场轮廓图

Fig. 2 Distribution of first 4-order-mode field of no-core fiber under different ZnO film thicknesses. (a) Variation of mode field with no-core fiber radius; (b) contour map of mode fields

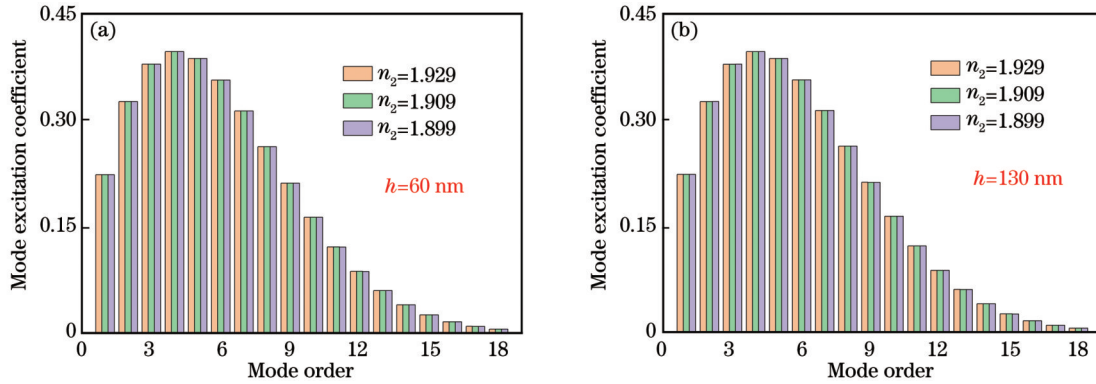


图 3 不同 ZnO 膜厚下无芯光纤的模式激发系数。(a) $h=60\text{ nm}$; (b) $h=130\text{ nm}$

Fig. 3 Mode excitation coefficient of no-core fiber under different ZnO film thicknesses. (a) $h=60\text{ nm}$; (b) $h=130\text{ nm}$

激发系数随 ZnO 膜层折射率的变化很小。当模式阶数 $m \leq 5$ 时, 相同模式下的模式激发系数随 ZnO 折射率的减小而增大; 当模式阶数 $m > 5$ 时, 变化趋势相反。

为进一步确定 SNS 传感器中无芯光纤的最佳长度, 分析了无芯光纤中干涉场自映像效应点的位置^[35]。图 4 是通过仿真得到的不同 ZnO 膜厚下无芯光纤中光

传输的模式干涉场分布情况, 可见: 膜厚为 60 nm 和 130 nm 时自映像长度分别为 58.43 mm 和 58.58 mm; 当 ZnO 膜层折射率减小为 1.889 时, 自映像长度分别为 58.45 mm 和 58.61 mm, 变化量非常小。各图中的对应插图是自映像点的局部放大图, 插图显示干涉场与入射光场的能量几乎一致, 说明此无芯光纤长度下 SNS 传感器的归一化透过率接近 1。

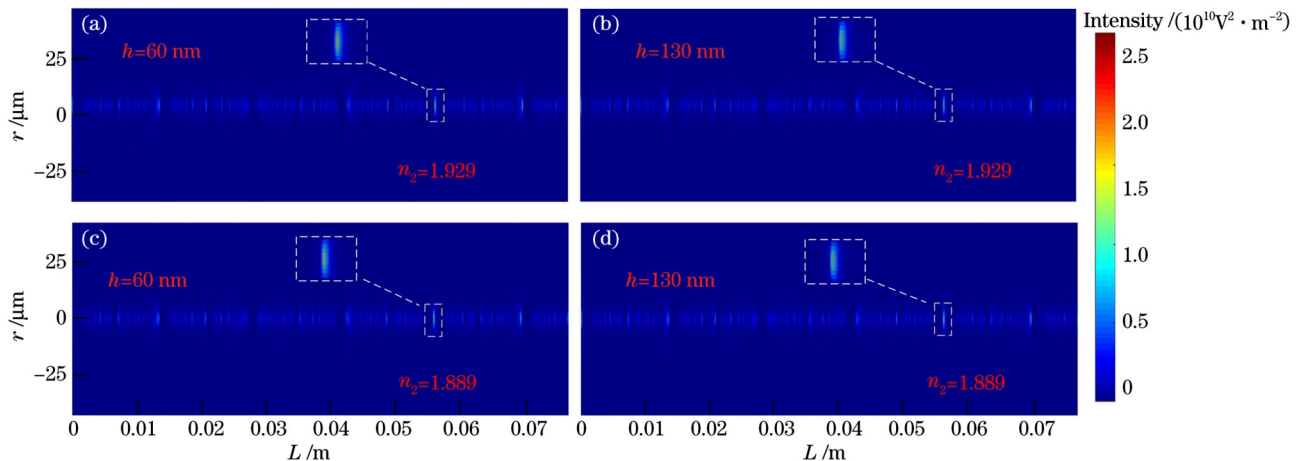


图 4 不同 ZnO 膜厚下无芯光纤中光传输的模式干涉场。(a)(c) $h=60\text{ nm}$; (b)(d) $h=130\text{ nm}$

Fig. 4 Mode interference field in no-core fiber under different ZnO film thicknesses. (a)(c) $h=60\text{ nm}$; (b)(d) $h=130\text{ nm}$

为了与制备的传感器中无芯光纤的长度保持一致, 选取无芯光纤长度为 58.19 mm 的 SNS 传感结构

进行透射谱仿真分析。60 nm 和 130 nm 膜厚下 SNS 传感器随 ZnO 膜层折射率变化的透射谱如图 5(a)、

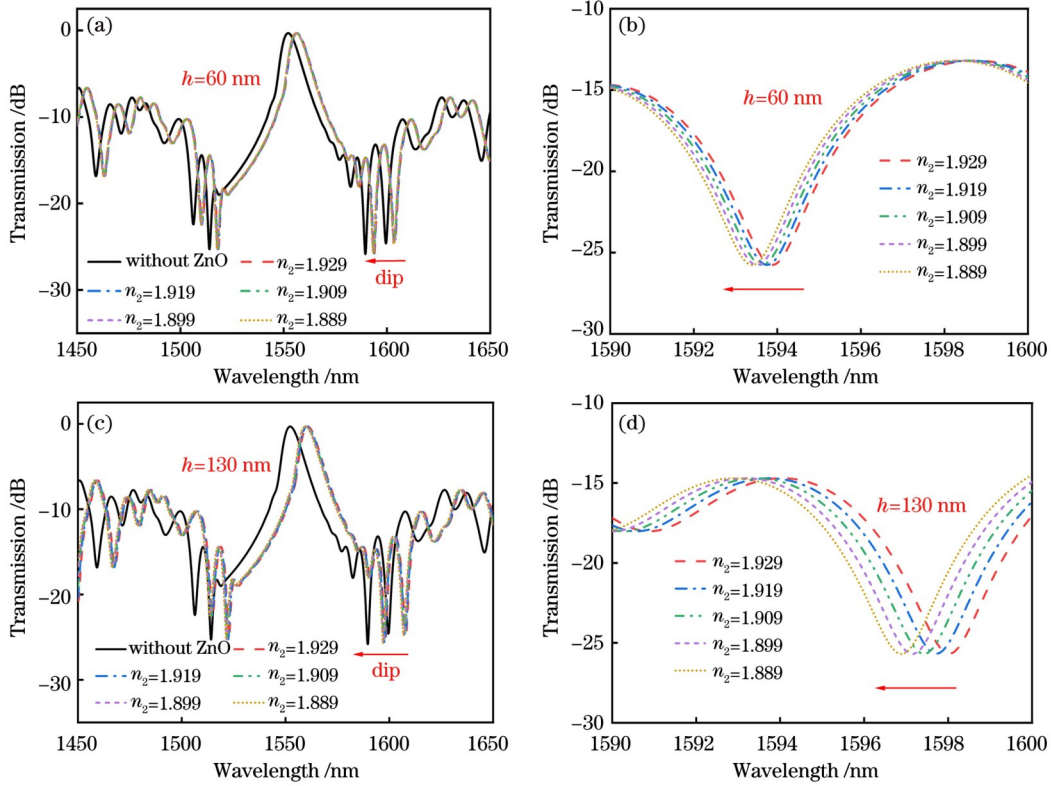


图 5 不同 ZnO 膜厚及不同 ZnO 折射率下的透射谱。(a) $h=60$ nm 下的透射谱;(b) $h=60$ nm 下干涉谷 dip 的放大图;(c) $h=130$ nm 下的透射谱;(d) $h=130$ nm 下干涉谷 dip 的放大图

Fig. 5 Transmission spectra under different ZnO film thicknesses and different ZnO refractive indexes. (a) Transmission spectra at $h=60$ nm; (b) enlarged view of interference valley dip at $h=60$ nm; (c) transmission spectra at $h=130$ nm; (d) enlarged view of interference valley dip at $h=130$ nm

(c) 所示,可以观察到自映像点对应的谐振波长位于 1550 nm 附近,其中,黑色实线是无 ZnO 膜层时 SNS 传感器的透射谱,涂覆 ZnO 薄膜后谐振波长发生红移。图 5(b)、(d) 分别展示了 1594 nm 和 1598 nm 附近干涉波谷 dip 的谐振波长放大图,可以清楚地看到谐振波长随 ZnO 膜层折射率减小发生了蓝移。

对图 5 中 dip 的谐振波长进行线性拟合,得到了不同 ZnO 膜层折射率下谐振波长的偏移量,如图 6 所示。ZnO 膜厚为 60 nm 和 130 nm 时,其灵敏度分别为 11.8 nm/RIU 和 28.6 nm/RIU。由此可知,ZnO 膜层

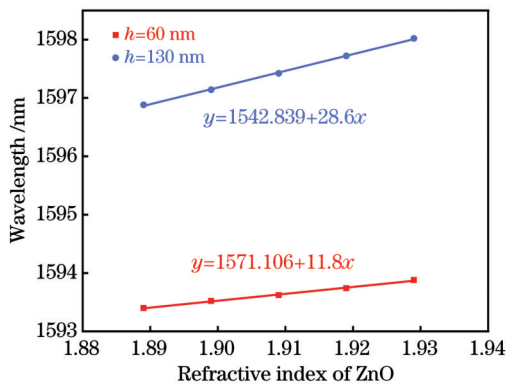


图 6 不同 ZnO 折射率下谐振波长的偏移量

Fig. 6 Shifts of resonant wavelength under different ZnO refractive indexes

越厚,其灵敏度越高。以上仿真为本文 NH_3 体积分数检测实验提供了一定的理论支撑。

3 实验与分析

3.1 传感器的制作

精确切割一段无芯光纤,测得其长度为 58.19 mm,再利用光纤熔接机(S179, FITELE)在无芯光纤两瑞端接单模光纤,获得 SNS 传感器。采用去离子水对制备好的 SNS 元件表面进行超声清洗,然后利用原子层沉积(ALD)技术无芯光纤表面沉积 ZnO 薄膜。在沉积实验中,以二乙基锌作为锌源的前驱体源,以去离子水作为氧源的前驱体源,采用纯度为 99.99% 的高纯氮气对反应腔进行吹扫(保证腔内清洁)。依次将锌源的前驱体材料和氧源的前驱体材料通入 ALD 反应腔室内,交替时间为 0.2 s,且每隔 2 s 通入氮气进行吹扫,以清除副产物和残留物。ALD 生长过程中保持温度为 200 $^{\circ}\text{C}$,通过控制生长循环次数最终在无芯光纤表面沉积一层厚度均匀的 ZnO 薄膜。使用场发射扫描电镜(JSM-7500F)对涂覆 ZnO 后的无芯光纤端面及表面进行拍摄,由图 7(a)所示的放大插图可知 ZnO 薄膜的厚度约为 60 nm,由图 7(b)所示的放大插图可知 ZnO 薄膜的微观形貌呈米粒状,薄膜具有良好的致密性和均匀性^[36]。

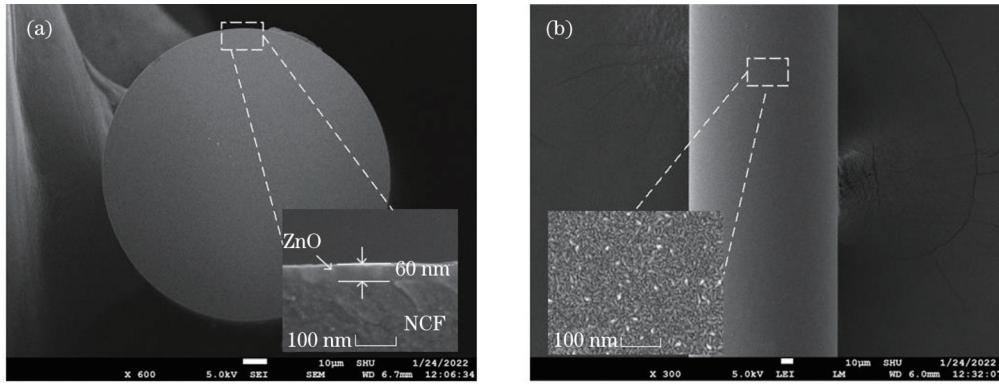


图7 ZnO膜层的电镜扫描测试结果。(a)端面形貌;(b)表面形貌

Fig. 7 Scanning electron microscope test results of ZnO film. (a) End face morphology; (b) surface morphology

3.2 实验系统搭建

搭建的NH₃检测装置结构示意图和实物图如图8(a)、(b)所示,该实验系统主要由光源、玻璃气室、光谱仪组成。SC-5-FC超连续宽带光源输出480~2200 nm波长范围的宽带光,光波通过SMF1传输至传感元件,传感元件水平放置在玻璃气室中,最终光波通过SMF2传输到AQ6370D光谱仪(OSA)进行光谱测量。玻璃气室配有进气口和出气口。在实验过程中,先将纯氮气通入玻璃气室中,持续通入3 min,以排净室内空气,然后以2 L/min的流量通入待测NH₃并维持4 min,以排净室内氮气,最终使玻璃气室内的NH₃体积分数与待测NH₃体积分数尽可能一致。

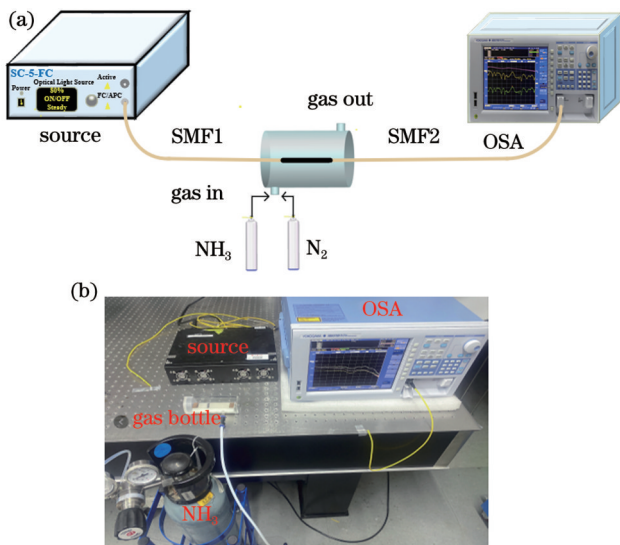


图8 NH₃传感装置。(a)结构示意图;(b)实物图

Fig. 8 NH₃ sensing device. (a) Structure diagram; (b) setup

3.3 NH₃传感实验

实验环境温度为16.5℃,NH₃体积分数为0、9.7×10⁻⁶、20.9×10⁻⁶、33.4×10⁻⁶、42.0×10⁻⁶的混合气体(NH₃与氮气的混合气体)由上海通辉特种气体有限公司提供。图9(a)、(c)分别为不同ZnO膜厚(60 nm和130 nm)下SNS传感器的透射谱,黑色线为未涂覆ZnO时的透射谱。可见,涂覆ZnO后透射谱的损耗增

大。选取两种膜厚下谐振波长分别在1590.3 nm和1591.9 nm附近的干涉波谷dip进行分析,分析结果如图9(b)、(d)所示。谐振波长随着NH₃体积分数的增加发生蓝移,当NH₃的体积分数从0增大到42.0×10⁻⁶时,60 nm和130 nm膜厚下的灵敏度分别为17.96×10⁶ pm和17.86×10⁶ pm。从仿真结果可知传感器灵敏度随着ZnO膜厚的增加而增大,而实验结果显示两种膜厚下SNS传感器的灵敏度相差不大,这主要是由ZnO对NH₃的吸附饱和^[32]造成的。因此,膜厚的无限增加并不能有效提高灵敏度,并且光能损耗也会随着膜厚增大而进一步增加,但仿真中并没有考虑此因素。基于以上分析,以下实验选择ZnO膜厚为60 nm的SNS传感器进行分析。

对60 nm膜厚下的SNS传感器每隔7天进行一次NH₃传感实验,不同NH₃体积分数下谐振波长的偏移量如图10(a)所示。其中实线是4次NH₃实验测试数据平均值的线性拟合结果,SNS传感器对NH₃检测的平均灵敏度为16.87×10⁶ pm,线性度为0.97159。由谐振波长的实验数据分析可知,当NH₃的体积分数为42.0×10⁻⁶时,吸附NH₃后的ZnO膜层的折射率变化量约为0.06,理论分析得到的膜层折射率的变化量(0.04)处于0~0.06范围内。对图10(a)中的拟合曲线进行换算,获得了实际测量NH₃体积分数与标准NH₃体积分数之间的关系,如图10(b)所示,计算得到两者的标准偏差为1.055×10⁻⁶,通过Hubaux-Vos法^[37]求得该传感器对NH₃的检测限 $x_D=6.6\times 10^{-6}$ 。进一步计算可以得到时间对NH₃检测限的影响为0.026×10⁻⁶ d⁻¹。

选取NH₃体积分数为42.0×10⁻⁶的混合气体对该传感器进行响应时间和恢复时间分析。首先,将上述气体匀速通入玻璃气室中,直到谐振波长稳定,得到传感器的响应时间;然后,向玻璃气室内匀速地通入氮气(以清扫NH₃),直到谐振波长恢复至原始位置,得到传感器的恢复时间。在此过程中,光谱仪每隔10 s记录一组数据,获取不同时刻的谐振波长,如图11所示。实验结果表明该传感器的响应时间 t_i 为70 s,恢复时间 t_r 为90 s。

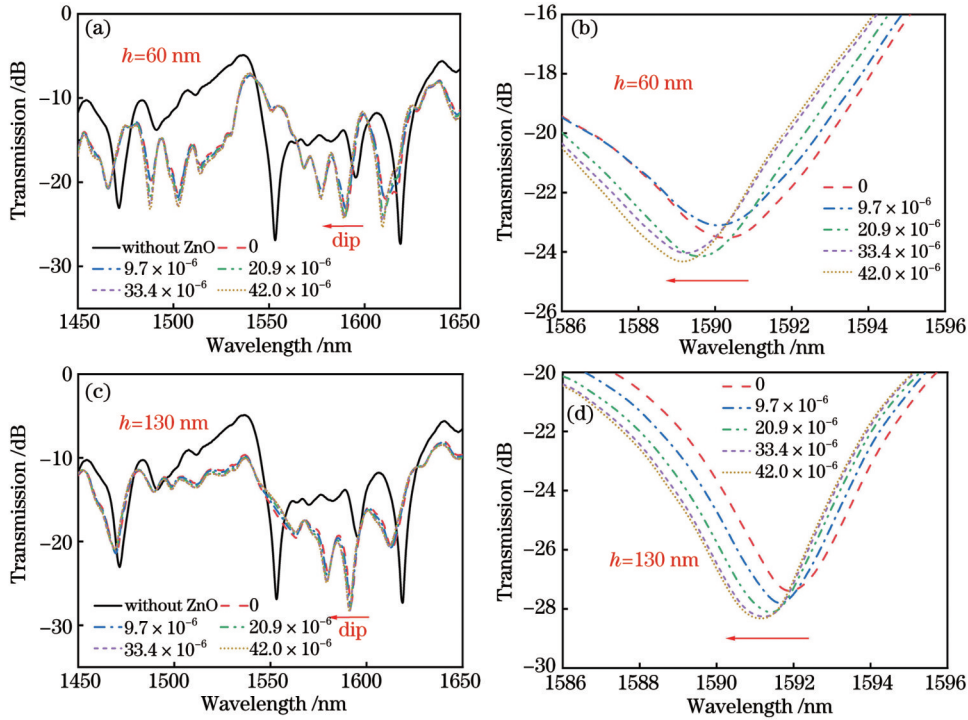


图 9 不同 ZnO 膜厚及不同 NH_3 体积分数下的透射谱。(a) $h=60$ nm 下的透射谱;(b) $h=60$ nm 下干涉谷 dip 的放大图;(c) $h=130$ nm 下的透射谱;(d) $h=130$ nm 下干涉谷 dip 的放大图

Fig. 9 Transmission spectra under different ZnO film thicknesses and different NH_3 volume fractions. (a) Transmission spectra at $h=60$ nm; (b) magnification of interference valley dip at $h=60$ nm; (c) transmission spectra at $h=130$ nm; (d) magnification of interference valley dip at $h=130$ nm

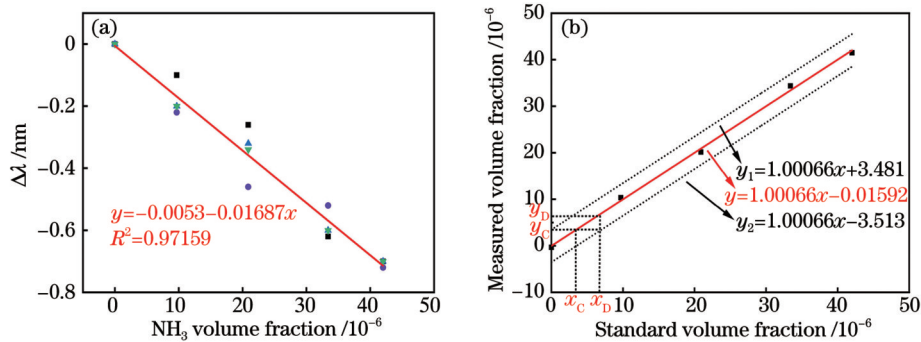


图 10 不同 NH_3 体积分数下谐振波长的偏移量。(a) 谐振波长偏移量随 NH_3 体积分数的变化;(b) NH_3 测量体积分数与标准体积分数之间的关系

Fig. 10 Resonant wavelength shift under different NH_3 volume fractions. (a) Variation of resonant wavelength shift with NH_3 volume fraction; (b) relationship between measured and standard NH_3 volume fractions

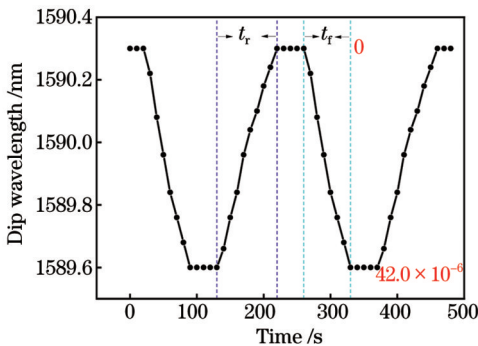


图 11 SNS 传感器对 NH_3 检测的响应-恢复曲线

Fig. 11 Response-recovery curve of SNS sensor for NH_3 detection

3.4 温度对 NH_3 传感的影响

实际的 NH_3 检测环境非常复杂,其中温度是一个重要的影响因素,因此需要进一步研究 SNS 传感器对 NH_3 检测的温度特性。将玻璃气室放入 GPG-4 型温控箱内,同时将 54IIB 型热电偶放置在玻璃气室的出气孔处,记录气室内的实际温度。图 12(a)是 NH_3 体积分数为 42.0×10^{-6} 时不同温度下的透射谱。可以看出:随着温度升高,干涉波谷 dip 的谐振波长发生红移,干涉波谷的幅值也发生了一定变化。测得不同温度下 SNS 传感器对 NH_3 检测的灵敏度如图 12(b)所示,在 16.5、25、30、45.2、56 $^\circ\text{C}$ 下, SNS 传感器对 NH_3 检测的灵敏度分别为 17.96×10^6 、 15.38×10^6 、 14.07×10^6 、

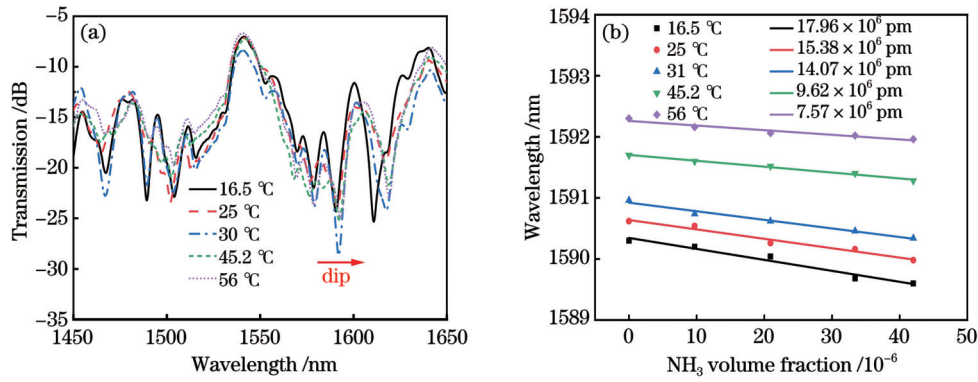


图 12 温度对 NH_3 检测的影响。(a) 不同温度下 SNS 传感器的透射谱; (b) 不同温度下 SNS 传感器对 NH_3 检测的灵敏度
Fig. 12 Effect of temperature on NH_3 detection. (a) Transmission spectra of SNS sensor at different temperatures; (b) sensitivity of SNS sensor for NH_3 detection at different temperatures

9.62×10^6 、 7.57×10^6 pm, 通过计算得到温度对 NH_3 检测限的影响为 $0.0237 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ 。灵敏度随温度升高而减小的主要原因如下: 温度升高时, 氧原子被吸附在带负电荷的 ZnO 表面, 电子被转移到吸附氧上, 氧原子就变成了氧负离子, 同时表面形成一个正的空间电荷层, 导致表面势垒升高, 阻碍了电子流动^[38], 最终导致 ZnO 膜层对 NH_3 的吸附能力降低。在实际的传感应用中, 环境温度对 NH_3 检测结果的影响不能忽略, 需要首先测得环境温度, 然后再根据数据插值法计算出 NH_3 的体积分数。

最后, 对近年来的 NH_3 传感研究结果^[9,16-17,39] 进行汇总比较, 如表 1 所示。表中数据表明: 采用复合材料制备的光纤传感器对 NH_3 的检测灵敏度可达到 27×10^6 pm, 虽然这一结果高于本传感器的检测灵敏度 17.96×10^6 pm, 但二者基本处于同一级别, 而且二者的响应时间和恢复时间几乎一致。后续研究可以从以下两个方面进行优化: 一是选择更高灵敏度的气敏材料制备 SNS 传感器; 二是对无芯光纤进行微加工, 使模式场对外界待测气体的变化更敏感, 由此进一步提高对 NH_3 检测的灵敏度。

表 1 各类 NH_3 传感器的性能比较

Table 1 Performance comparison of various NH_3 sensors

Sensor structure	Sensing material	Sensitivity / (10^6 pm)	t_r / s	t_r / s
TMMF ^[9]	Silica-gel	14.8	32	19.5
TSMF ^[39]	GO-Pt	10.2	30	100
MZI ^[16]	Graphene	3		
TCF ^[17]	PAA/PAH	27	70	80
Proposed sensor	ZnO	17.96	70	90

4 结 论

本文提出了一种基于 ZnO 涂层 SNS 光纤结构的高灵敏度 NH_3 传感器。对不同 ZnO 膜厚下的 SNS 传感器进行了仿真, 结果表明: 涂覆 ZnO 后无芯光纤中

的模场分布趋势一致, ZnO 膜层折射率从 1.929 变化至 1.889 时对激发系数和自映像长度的影响甚微; 传感器的灵敏度随膜厚的增加而增大, 60 nm 和 130 nm ZnO 膜厚下 SNS 传感器的灵敏度分别为 11.8 nm/RIU 和 28.6 nm/RIU。

采用 ALD 技术在 SNS 传感器上制备了厚度分别为 60 nm 和 130 nm 的 ZnO 薄膜, 两种膜厚下传感器对 NH_3 的检测灵敏度基本相同, 分别为 17.96×10^6 pm 和 17.86×10^6 pm, 这主要是由 ZnO 对 NH_3 吸附饱和导致的。进一步, 采用 ZnO 膜厚为 60 nm 的 SNS 传感器进行 NH_3 检测, 检测的平均灵敏度为 16.87×10^6 pm, 检测限为 6.6×10^{-6} , 响应时间和恢复时间分别为 70 s 和 90 s。最后, 对该传感器灵敏度的温度特性进行深入分析后发现, 该传感器对 NH_3 检测的灵敏度随着温度升高而降低, 当温度为 56 $^\circ\text{C}$ 时, 检测灵敏度降至 7.57×10^6 pm; 温度和时间对 NH_3 检测限的影响分别为 $0.0237 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ 和 $0.026 \times 10^{-6} \text{ } \text{d}^{-1}$ 。

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Ammonia Gas Sensor Based on No-Core Fiber Coated with Zinc Oxide

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Abstract

Objective With the rapid development of global industry, air pollution is now a major problem. Ammonia (NH_3) is a common toxic and harmful gas that is used in industrial production. Excessive intake of NH_3 by the human body can lead to lung swelling and even death. Currently, NH_3 detection is mainly conducted using electrochemical and optical methods. However, traditional electrochemical detection methods cannot realize real-time online monitoring. Optical detection can be classified into three types: absorption-spectrum, evanescent-wave, and refractive index variation. The absorption-spectrum type is easily affected by other gases in the same absorption band, whereas the evanescent-wave type has high requirements for achieving a precise tapering process. The refractive index variation type is based on variations in the refractive index of the sensitive film derived from NH_3 . In recent years, sensing technology that combines optical fiber sensors and functional films for realizing specific gas detection has become a research hotspot. Because zinc oxide (ZnO) has strong adsorption characteristics for NH_3 , the refractive index of ZnO varies. A no-core fiber is an optical waveguide with a unique structure, and its mode field can directly perceive changes in the external environment. Therefore, a new fiber gas sensor that combines a no-core fiber and ZnO film is studied in depth, which significantly promotes the rapid and accurate measurement of NH_3 in atmospheric pollutants.

Methods Based on mode transmission theory, the mode characteristics of a ZnO-coated no-core fiber and the sensing characteristics of a singlemode-no-core-singlemode (SNS) structure were analyzed using MATLAB software. First, the mode field distribution in the no-core fiber coated with ZnO was studied, and variations of the refractive index of the ZnO film with mode excitation coefficient and self-image length were discussed. Second, the relationship between the refractive index of the ZnO film and resonant wavelength of the interference spectrum was established. The NH_3 sensing system mainly includes a light source, glass chamber, and spectrometer. Finally, in an experiment, different volume fractions of NH_3 were passed into the glass chamber to ensure the sensor made full contact with NH_3 . When ZnO absorbs NH_3 , its refractive index changes, and thus the resonant wavelength shifts. In our study, NH_3 volume fraction was detected by establishing the relationship between the NH_3 volume fraction and the shift in resonant wavelength. The detection limit of the sensor was calculated using the Hubaux-Vos method, and the response time and recovery time were tested. In addition, the ambient temperature was controlled using a temperature-control box to study the effect of temperature on NH_3 sensing.

Results and Discussions Changes in the refractive index of a ZnO film affect to some degree the mode excitation coefficient and self-image length in a no-core fiber coated with a ZnO film layer. The sensitivity of the sensor increases with increasing film thickness. In our study, the sensitivities of the SNS sensor with thicknesses of 60 nm and 130 nm are 11.8 and 28.6 nm/RIU, respectively (Fig. 6). The prepared ZnO film was characterized using scanning electron microscopy (SEM), and the results show good compactness and uniformity (Fig. 7). At 16.5 °C, the resonant wavelength blue-shifts with an increase in NH_3 volume fraction. The sensitivities of the SNS sensor at ZnO film thicknesses of 60 and 130 nm are 17.96×10^6 and 17.86×10^6 pm, respectively, which is mainly caused by the effects of ZnO on NH_3 adsorption saturation (Fig. 9). The average sensitivity of the SNS sensor under NH_3 detection coated with a ZnO film at a thickness of 60 nm is 16.87×10^6 pm, and the detection limit is 6.6×10^{-6} (Fig. 10). The effect of time on the detection limit is $0.026 \times 10^{-6} \text{ d}^{-1}$, and the response and recovery time are 70 and 90 s, respectively (Fig. 11). The sensitivities of the sensor under NH_3 detection are 17.96×10^6 , 15.38×10^6 , 14.07×10^6 , 9.62×10^6 , and 7.57×10^6 pm at 16.5, 25, 30, 45.2, and 56 °C, respectively (Fig. 12). The effect of temperature on the detection limit is $0.0237 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. The detection sensitivity of NH_3 decreases with an increase in temperature, which derives from the fact that the increase in the surface potential barrier of the ZnO film hinders the flow of electrons. In practical sensing applications, measuring the temperature of the environment is first required, and then the volume fraction of NH_3 can be calculated based on the data interpolation.

Conclusions A high-sensitivity NH_3 sensor based on a ZnO-coated SNS structure was proposed in this study. SNS sensors with different ZnO film thicknesses were simulated theoretically. The results show that the mode field distribution trend of the no-core fiber coated with ZnO is consistent. When the refractive index of the ZnO film changes from 1.929 to 1.889, it has little effect on the excitation coefficient and self-image length. In general, the sensitivity of an SNS sensor increases with an increase in film thickness. In this study, an SNS sensor with ZnO film thicknesses of 60 and 130 nm was prepared by atomic layer deposition (ALD), with results showing sensitivities of 11.8 and 28.6 nm/RIU, respectively. The results show that the sensitivities to NH_3 are essentially the same under the two film thicknesses (17.96×10^6 and 17.86×10^6 pm, respectively), which mainly derives from the effects of ZnO on NH_3 adsorption saturation. The average sensitivity, detection limit, and response and recovery time are 16.87×10^6 pm, 6.6×10^{-6} , and 70 and 90 s, respectively. Finally, an in-depth analysis of the temperature characteristics of the sensitivity of the sensor demonstrated that NH_3 detection sensitivity decreases with an increase in temperature. At 56 °C, the sensitivity decreases to 7.57×10^6 pm. The effects of temperature and time on the detection limit of NH_3 are $0.0237 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $0.026 \times 10^{-6} \text{ d}^{-1}$, respectively.

Key words sensor; no-core fiber; zinc oxide; ammonia measurement; temperature