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基于钽基氢气传感薄膜的新型光纤传感技术

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摘 要:设计基于钽基氢气传感薄膜的新型光纤氢气传感系统,采用本征具有3~4 nm平坦区域的放大自发辐射光源作为传感光源,利用相位掩模法在单模光纤中刻写中心波长位于光源平坦区域的高反射率光栅,采用磁控溅射方法在单模光纤端面沉积40 nm $Ta_{0.88}Pd_{0.12}$~10 nm Pd~6 nm Pt~40 nm PTFE多层纳米复合薄膜制备微反射镜型氢气传感探头。高反射光栅的反射峰强度(I_1)几乎不受氢气传感薄膜反射率影响,其峰值作为参考信号;高反射光栅附近的背底强度(I_2)受氢气传感薄膜反射率影响,其强度作为传感信号。通过高反射光栅的反射峰强度(I_1)与背底光强度(I_2)的比值监测氢气浓度,可以大幅提升系统信噪比。利用氮气作为载气对传感探头进行氢敏性能测试,实验结果表明传感探头具有较好的重复性和稳定性,并且在低浓度氢气下传感探头灵敏度较好。该传感探头具有在无氧环境下监测氢气浓度的潜力。

关键词:光纤传感;氢气监测;TaPd复合膜;无氧环境;磁控溅射
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0 引言

氢能作为绿色能源,由于其清洁,便于储存和资源丰富的特点,在未来可持续能源中占有重要地位。氢气与传统能源如天然气、液化石油气及汽油一样,不仅具有较高的能量,也具有一定的爆燃风险(浓度>4%)。一些重要设施,如电力变压器[1]和核材料存贮容器[2],氢浓度是评估其健康状态的重要指标,这就需要能够在无氧环境中正常工作的氢气传感器。

氢气传感器按照工作原理可以分为半导体型氢气传感器[3]、电化学型氢气传感器[4]、热电型氢气传感器[5]、光纤型氢气传感器等。其中半导体型氢气传感器、电化学型氢气传感器、热电型氢气传感器对工作温度要求高(部分需要几百度的高温)容易产生电火花,存在安全隐患。光纤型氢气传感器在光纤中采用微弱的光信号作为传感信号,具有体积小、本质安全和抗电磁干扰等优点,可以在常温下使用,避免产生电火花引发氢气爆炸。光纤氢气传感器的原理是将光纤与氢气传感材料结合,氢气传感材料遇氢气发生反应,吸氢后会产生氢致变色效应[6]和热效应[7-9],导致光纤中的光信号发生变化,根据光信号的变化对氢气浓度进行监测。

已有报道[7-9]将成分为WO_3的氢气传感材料涂覆在光纤光栅周围制备氢气传感器,氢气传感材料与氢气反应会产生热量,改变光纤光栅周围的温度,导致光栅的中心波长改变,根据光栅中心波长的变化来计算氢气浓度。通过将WO_3[10]或镁[11]的复合膜沉积在光纤端面制备微反射镜型光纤氢气传感器,利用WO_3或镁

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合金薄膜的氢致变色效应会引起反射光强度变化的原理来监测氢气。WO_3基和镁基氢气传感薄膜需要在氧气的存在下才能进行重复性测试，只适用于在空气中进行氢气浓度监测。在无氧环境下能够重复性测试的传感薄膜还有待进一步研究。

1 基本原理

金属钯常被应用于氢气传感，对氢气具有灵敏度高和选择性强的优点，能够吸收自身体积900倍的氢气[12]。钯与氢气反应的机理是在常温下将氢气分子解离为氢原子，氢原子与钯反应生成钯的氢化物PdH_x，当氢气消失时PdH_x分解生成Pd。氢气浓度过高时，PdH_x发生一级相变，从α-PdH_x相转变为β-PdH_x相[6]。纯钯薄膜的α、β相晶格参数差异很大，导致两种晶相的转化会产生一定的内应力，使响应时间相对较长，薄膜容易出现明显的开裂和脱落现象[6]。

研究表明，当往钯中加入Au[13-15]、Ni[16]、Ag[17-18]、Cu[19]等元素形成合金时，能够抑制钯的α相和β相的转变，消除相变引起的薄膜开裂现象。钽的性质稳定，对氢气的溶解度高[20]。采用TaPd复合膜不仅可以克服纯钯薄膜的氢脆现象，而且在无氧环境下其氢敏性能良好，该氢气传感薄膜为制备无氧环境中光纤氢气传感器提供了新思路。由于文献[20]只研究TaPd复合膜在不同氢气浓度下透射率变化性能，并没有将其集成在光纤上，对氢气反应过程中反射率变化和以该薄膜为传感材料的光纤氢气传感探头的性能还有待进一步研究。本文通过在单模光纤端面沉积TaPd复合膜的方法制备微反射镜型光纤氢气传感探头，利用氮气作为载气研究传感探头在不同的氢气浓度下响应特性。钽、钯吸收氢气后变成TaH_x和PdH_x，导致薄膜的反射率变小，从而通过反射光强度的变化来监测氢气。

2 实验装置和数据分析

2.1 传感探头的制备和测试系统的设计

首先，用剥线钳去掉单模光纤的聚合物涂层；然后，切割去除涂覆层的光纤以形成平坦的截面，用于沉积氢气传感薄膜。接下来将切割好的光纤放入磁控溅射镀膜机的腔室内抽真空，将真空度抽到10^{-5} mbar级别，然后开始镀膜。在镀膜的过程中，先将钽靶材预溅射6 min去除靶材表面的氧化层，预溅射速率为0.06 nm/s。之后采用磁控共溅射制备TaPd复合薄膜，该过程中钽和钯溅射速率分别为0.09 nm/s和0.01 nm/s。随后再分别溅射钯和铂薄膜以防止钽氧化，两种薄膜的溅射速率分别为0.1 nm/s和0.12 nm/s。钯薄膜可以提高氢气传感薄膜的选择性[21]，铂作为保护层具有良好的催化效果和抗氧化能力[22]。最后再沉积聚四氟乙烯(Poly Tetra Fluoroethylene，PTFE)薄膜，溅射速率为0.02 nm/s。PTFE具有憎水性[23]，其吸水率一般在0.001%～0.005%左右，而且它的渗透率较低[24]，能阻碍水分子吸附在氢气传感薄膜表面。但是当环境湿度较高时，高湿度会对PTFE的稳定性产生影响[25]，传感探头适合在较低的湿度环境下使用。当环境温度小于300 ℃时，PTFE薄膜具有良好的温度稳定性[25]。因此本文选用PTFE作为氢气传感薄膜的最外层保护膜，减小温度和湿度对传感探头性能的影响。该氢气传感薄膜的膜系结构为40 nm $Ta_{0.88}Pd_{0.12}$～10 nm Pd～6 nm Pt～40 nm PTFE。将沉积传感薄膜的裸光纤插入玻璃点样毛细管，毛细管的外层先用聚合物软管包覆，然后用不锈钢管包覆，制成传感探头。不锈钢管的侧面有两个小孔，利于气体的交换，插入气室中即可进行传感探头的氢敏性能测试。

如图1所示，采用课题组搭建的传感系统对该探头的氢敏性能进行测试。放大自发辐射(Amplified Spontaneous Emission，ASE)光源发出的光经过光衰减器衰减后进入3 dB光纤耦合器，经光纤光栅和氢气传感薄膜反射后回到光纤耦合器，部分反射光通过光纤耦合器的另一端进入光谱采集模块(BaySpec，1 520～1 570 nm)。传感探头的反射光谱图如图2，红色线条是高反射光纤光栅的光谱图，黑色线条是沉积氢气传感薄膜的单模光纤接入光路中的光谱图，高反射光纤光栅的反射峰强度为I_1，其背底噪声强度为I_2，均读取自光谱采集模块提供的1 520～1 570 nm范围内的光谱数据，I_1的值通过寻峰算法获得，取光谱图中合适波长范围内光强平坦区域的平均值为I_2的值。由于光纤光栅的高反射率，反射峰强度(I_1)几乎不受氢气传感薄膜反射率影响，其峰值可作为参考信号。氢气传感薄膜与氢气反应时，氢气传感薄膜的反射强度发生变化，背底强度(I_2)也会随之发生改变，因此背底强度(I_2)可作为传感信号。这两类信号受到的光源波动、插

入损耗以及光纤弯曲所带来的影响相同，因此通过高反射光栅的反射峰强度I_1与背底光强度I_2的比值(I_1/I_2)监测氢气浓度，可以大幅提升系统信噪比[8]。

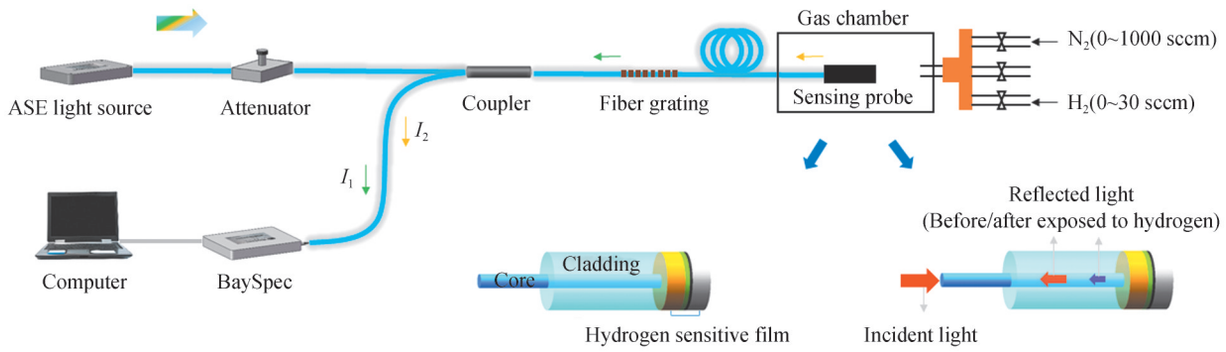


图 1　光纤氢气传感系统原理

Fig. 1　Schematic of the optical fiber hydrogen sensing system

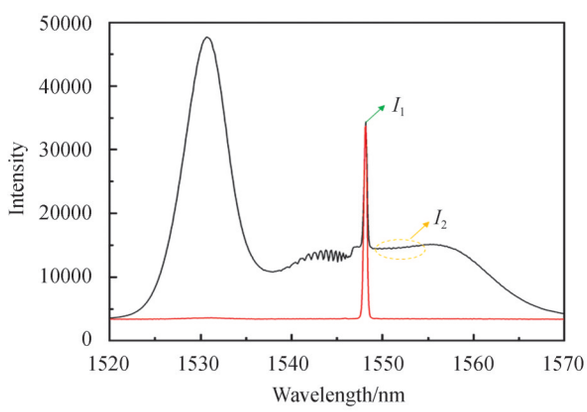


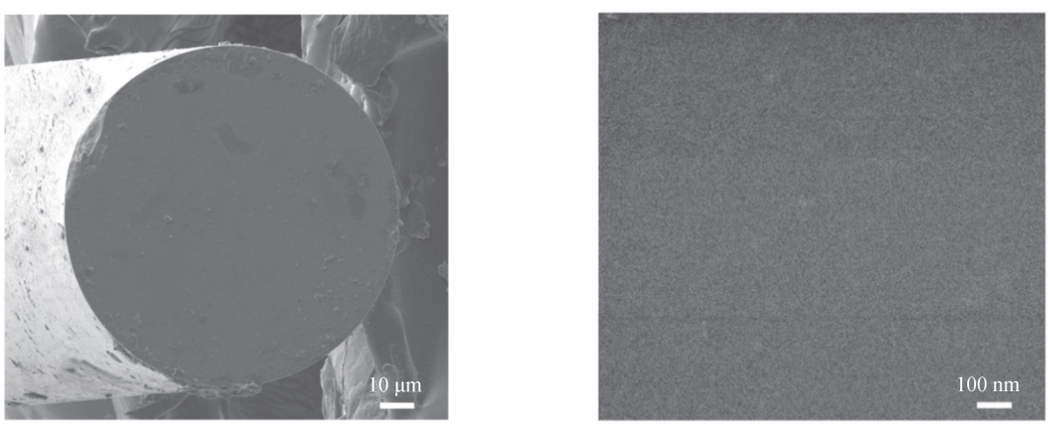
图 2　沉积氢气传感薄膜的单模光纤在接入前和接入后的系统光谱图

Fig. 2　System spectrograms of single mode fiber deposited with hydrogen sensing film before and after connection

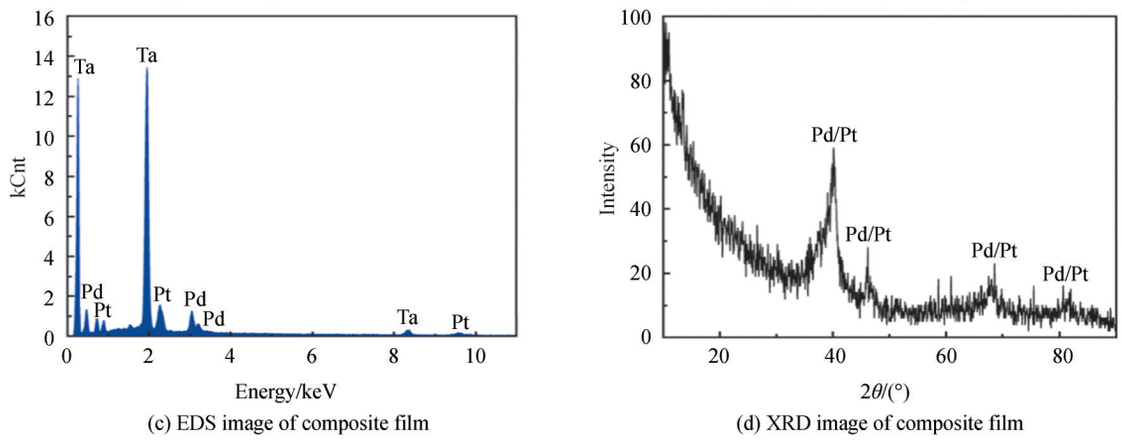
室温下，传感探头的氢敏性能测试是在纯N_2(99.99%)和纯H_2(99.99%)的混合气以及纯N_2(99.99%)和H_2、N_2体积比为1∶99的混合气中进行。通过两个流量计(北京七星华创，0～30 sccm、0～1 000 sccm)分别用来控制纯H_2(或H_2、N_2体积比为1∶99的混合气)和纯N_2的流量，通过改变这两个流量计的气体流量配比来调节氢气的浓度。在测试过程中，气体总流量保持在1 000 sccm，采集的光谱数据被计算机存储和处理。

2.2　实验结果和分析

图3(a)、(b)为氢气传感薄膜(通氢气后)的冷场发射扫描电子显微镜(Scanning Electron Microscope，SEM)图像。从图中可以看出，通氢气后薄膜表面的致密性和均匀性很好，并没有出现明显的微裂纹，表明



(a) SEM image of fiber end face　　(b) SEM image of composite film



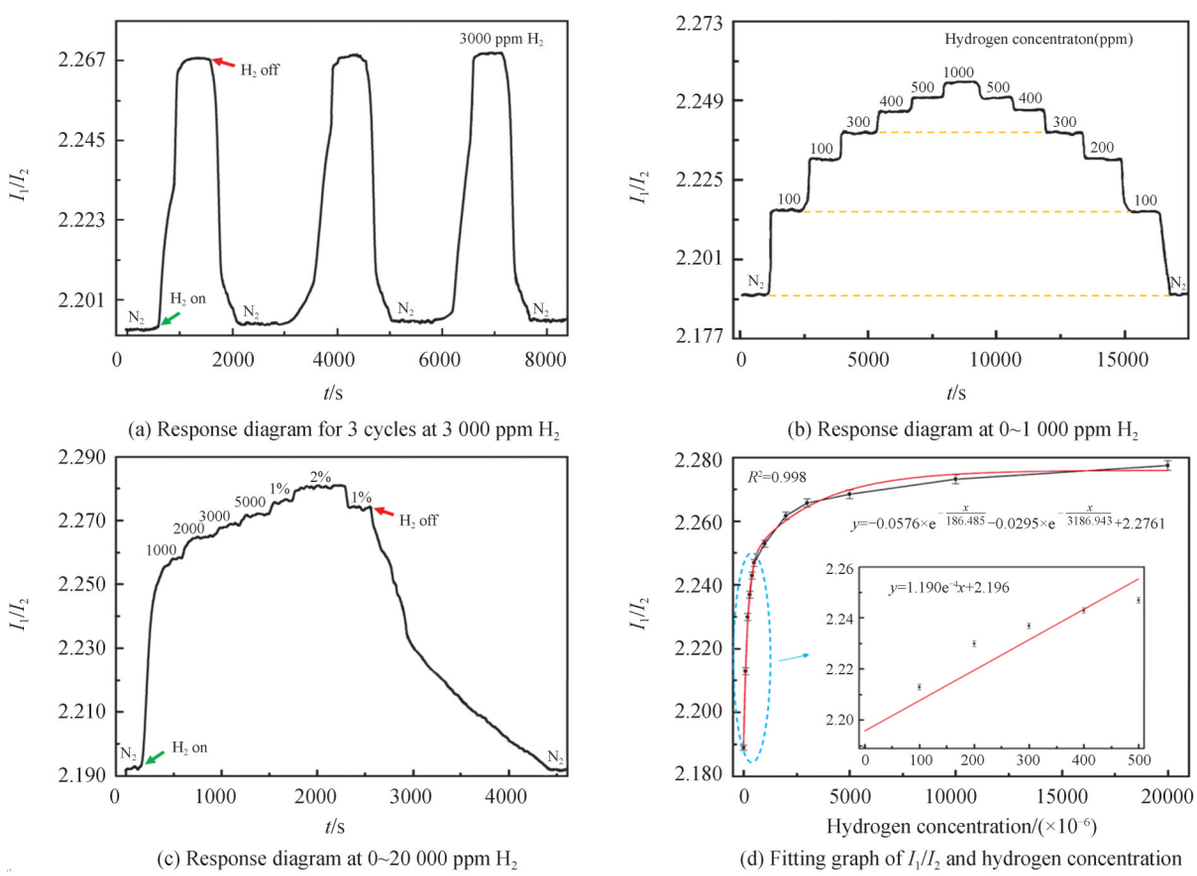
(c) EDS image of composite film　　(d) XRD image of composite film

图 3　传感探头材料表征图

Fig. 3　Sensing probe material characterization diagram

薄膜的机械性能良好。通过附着在冷场发射扫描电子显微镜上的能量色散X射线光谱仪(Energy Dispersive Spectrometer, EDS)对薄膜元素进行分析,从图3(c)可以看出Ta、Pd、Pt的原子比为69∶11∶20,与40 nm $Ta_{0.88}Pd_{0.12}$、10 nm Pd、6 nm Pt中Ta、Pd、Pt的实际原子比接近。图3(d)为该膜系结构的X射线衍射(X-ray Diffraction, XRD)相分析图,从图中可以观察到钯和铂的衍射峰,未观察到钽元素的特征峰,导致该现象的原因可能是钽以非晶相形式存在。

图4(a)为传感探头在3 000 ppm(1 ppm=1×10^{-6}) H_2下的三次循环测试响应,配气系统向气室中交替通入N_2和3 000 ppm H_2/N_2混合气。开始只通入N_2一段时间,强度比值I_1/I_2能保持稳定;然后通入3 000 ppm H_2,I_1/I_2上升到一定值后保持不变;随后通入纯N_2,待I_1/I_2下降到一个稳定值后开始第二、三个循环。从图中



(a) Response diagram for 3 cycles at 3 000 ppm H_2

(b) Response diagram at 0~1 000 ppm H_2

(c) Response diagram at 0~20 000 ppm H_2

(d) Fitting graph of I_1/I_2 and hydrogen concentration

图 4　传感探头氢敏性能测试图

Fig. 4　Hydrogen sensitivity test diagram of sensor probe

可以看出这三次循环的图像变化大致一致，这表明传感探头有着良好的重复性和稳定性。另外，传感探头在氮气中具有很好的恢复性，表明该传感探头适用于无氧环境下氢气浓度的监测。

实验中测试了传感探头在相对较低氢气浓度（1 000 ppm以内）连续变化下的响应曲线，该过程中采用纯N_2和H_2、N_2体积比为1∶99的混合气进行配气提供不同浓度氢气。如图4（b）所示，先通入N_2，待I_1/I_2稳定后，再分别通入100 ppm、200 ppm、300 ppm、400 ppm、500 ppm、1000 ppm H_2。与初始值相比，I_1/I_2的变化量分别是0.025、0.042、0.048、0.054、0.060、0.065。当氢气浓度逐次下降时，I_1/I_2的变化量分别是0.060、0.054、0.048、0.042、0.025，该现象表明传感探头对不同浓度氢气的响应均可保持稳定，表明该氢气传感薄膜的可靠性。传感探头在相对较高氢气浓度（大于1 000 ppm）连续变化下氢敏性能的测试采用纯N_2和纯H_2的混合气进行配气提供不同浓度氢气。如图4（c）所示，当氢气浓度分别是1 000 ppm、2 000 ppm、3 000 ppm、5 000 ppm、10 000 ppm、20 000 ppm时，I_1/I_2的变化量分别是0.066、0.073、0.077、0.080、0.084、0.089，验证了该传感探头在高浓度的氢气中也有很好的恢复性。

图4（d）显示了I_1/I_2在100 ppm～20 000 ppm H_2下的变化量，传感探头的非线性响应过程。从图中可以看出氢气浓度越高，该传感探头的灵敏度相对较低，主要是因为氢气传感薄膜在高浓度氢气下容易达到饱和。而传感探头在100 ppm～1 000 ppm低浓度氢气下灵敏度较高，I_1/I_2在几秒内波动可达0.001[8]，理论上分辨率可以达到20 ppm，因此该传感器适用于氢气浓度较低的场合。

3 结论

本文提出了一种基于40 nm $Ta_{0.88}Pd_{0.12}$～10 nm Pd～6 nm Pt～40 nm PTFE新型氢气传感膜系的光纤传感探头，传感探头在无氧环境下具有良好的重复性和恢复性。传感系统测得的强度比值I_1/I_2与氢气浓度一一对应，表明传感探头对氢气浓度敏感。因此本文研究的微反射镜型光纤氢气传感探头具有在无氧环境下监测氢气浓度的潜力。并且传感探头在较低的氢气浓度时具有更高的灵敏度，在100 ppm～1 000 ppm氢气范围内理论分辨率为20 ppm。

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Novel Optical Fiber Sensing Technology Based on Tantalum-based Hydrogen Sensing Film

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Abstract: Hydrogen is explosive and hydrogen sensors are used in hydrogen monitoring work. The hydrogen sensor films used in previous hydrogen monitoring work were WO_3-based and Mg-based hydrogen sensor films, which only available in an aerobic environment. Hydrogen sensing films for monitoring hydrogen concentration in an oxygen-free environment remain to be further investigated. Tantalum is stable in nature and has a high solubility for hydrogen in oxygen-free environment. In this paper, 40 nm $Ta_{0.88}Pd_{0.12}$～10 nm Pd～6 nm Pt～40 nm PTFE multilayer films were deposited on the end face of single mode optical fiber for hydrogen concentration monitoring for the absence of oxygen. The

reflectivity of the deposited film under different hydrogen concentration was probed by the sensing demodulator. The sensing performance were investigated by a series of hydrogen sensing experiments. Firstly, the sensing film are designed for hydrogen sensing in oxygen-free environment. The $Ta_{0.88}Pd_{0.12}$ thin film is used as basal layer for sensing. Palladium film can improve the selectivity of hydrogen sensing film. Tantalum and palladium absorb hydrogen and become TaH_x and PdH_x. This phenomenon will result in a decrease in the reflectivity of the film, so that hydrogen concentration can be monitored by the change of reflected light intensity. Platinum film has good catalytic effect and excellent oxidation resistance, so it is employed as a protective layer. PTFE is hydrophobic and can hinder the adsorption of water molecules on the surface of the hydrogen sensing film. Moreover, it has good stability under various ambient environment, which can reduce the negative influence of temperature and humidity. The hydrogen sensing probe was fabricated by magnetron sputtering aforementioned multilayer films. The microscopic morphology of hydrogen sensing film was characterized by scanning electron microscope. Elements of hydrogen sensing thin film were analyzed by energy dispersive spectrometer. The phases of hydrogen sensing film were analyzed by X-ray diffractometer. Secondly, a fiber optic hydrogen sensing system based on Ta-based hydrogen sensing film was constructed, including amplified spontaneous emission light source, attenuator, coupler, spectral acquisition module, reference fiber grating and the fabricated sensing probe. The spectral response of the reference fiber grating with high-reflection was acquired by a compact spectral acquisition module with the range of 1 520~1 570 nm. The Reflection peak intensity (I_1) and background intensity (I_2) were obtained simultaneously. Reflection peak intensity (I_1) of the high-reflection fiber grating is hardly affected by the reflectivity of hydrogen sensing film and is used as the reference signal. The ratio of I_1 over I_2 is traced as main measuring parameter to enhance the signal noise ratio of sensing system and to suppress the other noise induced by light source fluctuations, insertion loss, and fiber bending. Finally, we investigated the hydrogen sensing performance of the fabricated sensing probe. The probes are characterized in different hydrogen concentration provided by a gas mixer including two gas flow meters with N_2 as carrier gas. A series of experiments are carried out to verify the sensitivity and repeatability of the fiber optic hydrogen sensing system with the proposed Ta-based probe. Three on/off cycles under a hydrogen concentration of 3 000 ppm are conducted. When the sensor is put in nitrogen, the value of I_1/I_2 is on a lower level. When the hydrogen with a concentration of 3000 ppm is turned on, the value of I_1/I_2 rises to a higher value each time. The results have shown the sensor has a good repeatability and recovery during hydrogen on/off cycles. Multiple experiments under gradient hydrogen concentration with a lower range of 100 ppm~1 000 ppm and a higher range of 1 000 ppm~20 000 ppm show that the different hydrogen sensitivity for different hydrogen concentration ranges. When the hydrogen concentration is in the range of 100 ppm~1 000 ppm, the sensitivity of sensor probe is the largest. The theoretical resolution is 20 ppm in the range of 100 ppm~1 000 ppm hydrogen concentration. This is because the hydrogen sensing film can easily reach saturation in the absorption of hydrogen at high concentrations of hydrogen. As the hydrogen concentration increases over 1 000 ppm, the reaction rate of the sensing film with hydrogen becomes slower. The result implies the sensor probe presents better sensitivity towards lower hydrogen concentration. In conclusion, the sensor probe proposed in this paper has the potential to monitor hydrogen concentrations in an oxygen-free environment and is suitable for monitoring the change of low concentration hydrogen gas.

Key words: Fiber optic sensor; Hydrogen monitoring; TaPd composite film; Anaerobic environment; Magnetron sputtering

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