

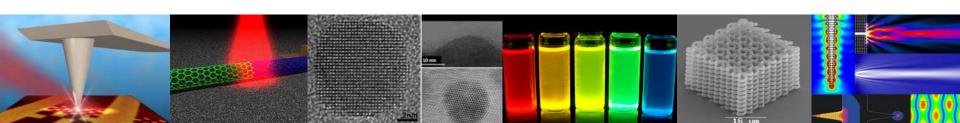
纳米光子学

Nanophotonics

第8讲:表面等离激元的激发与表征

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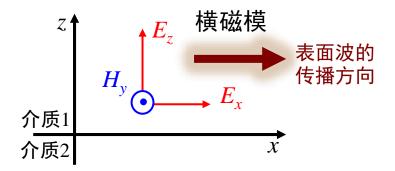


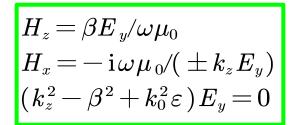
上讲回顾

从两个旋度方程+解的形式,得到两种模式的方程组

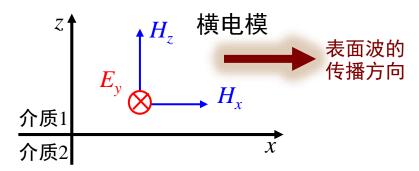
$$egin{aligned} E_{x}\!=\!\pm\,k_{z}H_{y}\!/\mathrm{i}\omegaarepsilon_{0}arepsilon\ E_{z}\!=\!-\,eta H_{y}\!/\omegaarepsilon_{0}arepsilon\ \left(k_{z}^{\,2}\!-\!eta^{2}\!+\!k_{0}^{\,2}arepsilon\,
ight)H_{y}\!=\!0 \end{aligned}$$

TM模式





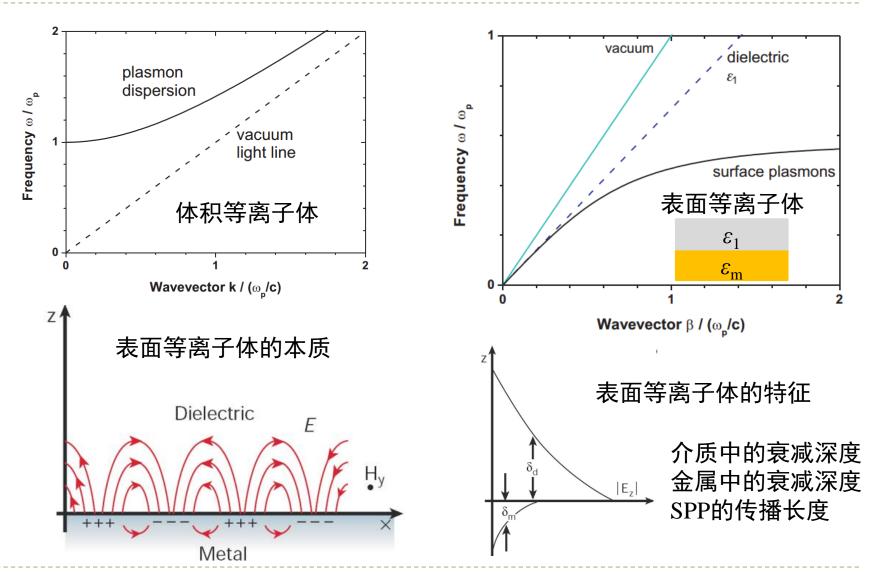
TE模式



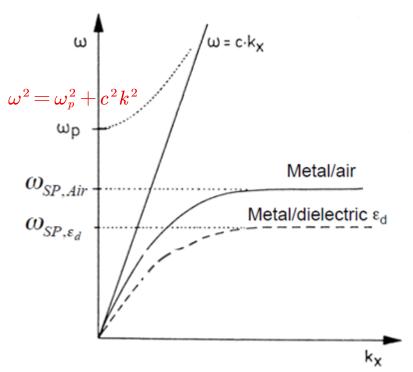
- TE模式: 界面附近方程无解, 不存在电磁表面波模式
- TM模式:界面附近方程有解,存在电磁表面波模式:表面等离极化激元(SPP)
- · SPP的色散关系:

$$eta = k_0 \sqrt{rac{arepsilon_m arepsilon_d}{arepsilon_m + arepsilon_d}}$$

上讲回顾



等离子体色散关系



$$\varepsilon_m(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

$$\beta = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$

$$\omega = \omega_{\rm sp} \ {\rm when:} \\ \varepsilon_m = 1 - \frac{\omega_p^2}{\omega^2} = -\varepsilon_d \Longrightarrow \omega^2 - \omega_p^2 = -\varepsilon_d \omega^2 \Longrightarrow \omega^2 = \frac{\omega_p^2}{1 + \varepsilon_d} \Longrightarrow \omega = \frac{\omega_p}{\sqrt{1 + \varepsilon_d}}$$

介质折射率越高对应 $\omega_{\rm sp}$ 越小

等离子体光学

- 金属光学与体积等离激元
- ▶ 表面等离子体激元
- ▶ 表面等离子体激元的激发与表征
- 局域表面等离子体
- ▶ 等离子体集成电路

光照射金属表面激发SPP? 由于SPP位于金属表面,我们如何观察和检测?

本讲内容

▶ SPP的激发

- ▶ 1.1 棱镜耦合
- ▶ 1.2 通过高度集中的光束激发
- ▶ 1.3 光栅耦合
- ▶ 1.4 散射激发
- ▶ 1.5 近场激发
- ▶ 1.6 其它耦合方法

SPP的表征

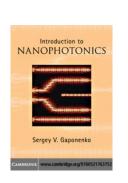
- ▶ 2.1 近场显微镜
- ▶ 2.2 泄漏辐射显微镜
- ▶ 2.3 荧光成像

守恒定律

The value,

$$p = \hbar k, \tag{4.12}$$

is called the "quasi-momentum". It differs from the momentum by a specific conservation law. It conserves with an accuracy of $2\pi\hbar/a$, which is, again, a direct consequence of the translational symmetry of space. The quasi-momentum conservation law is to be considered in line with the known conservation laws, namely momentum conservation (resulting from space homogeneity), energy conservation (resulting from time homogeneity) and circular momentum conservation (resulting from space isotropy), and all these conservation laws agree with the *Noether theorem*. This states that every type of space and time symmetry generates a certain conservation laws.





空间均匀——动量守恒时间均匀——能量守恒空间各向同性——角动量守恒

"Introduction to nanophotonics" written by Sergey V. Gaponenko

守恒定律——折射定律

The refraction of a light ray at an interface between two dielectrics ε_1 and ε_2 , illustrated in figure 4, is usually described in terms of **Snell's law**: $n_1 \sin \theta_1 =$ $n_2 \sin \theta_2$, where n_i is the refractive index $\sqrt{\varepsilon_i}$ and θ_i is the angle the ray makes with the normal to the interface. If $\theta_1 > \sin^{-1}(n_2/n_1)$, then the law would demand $\sin \theta_2 > 1$, for which there is no real solution; the interpretation is that the ray is totally reflected. The critical angle $\theta_c = \sin^{-1}(n_2/n_1)$ exists only for $n_2 < n_1$, so total internal reflection occurs only within the higher-index medium. Snell's law, however, is simply the combination of two conservation laws that follow from symmetry: conservation of frequency ω (from the linearity and time-invariance of the Maxwell equations), and conservation of the component k_{\parallel} of **k** that is parallel to the interface (from the continuous translational symmetry along the interface, as we noted above). In particular, $k_{\parallel} = |\mathbf{k}| \sin \theta$, and $|\mathbf{k}| = n\omega/c$ from the dispersion relation. We obtain Snell's law by setting k_{\parallel} equal on both sides of the interface. The advantage of this way of thinking about the problem is that we are now in a position to generalize beyond the ray-optics regime (which is valid only on length scales much larger than the wavelength of light).

"Photonic Crystals: Molding the flow of light" written by John D. Joannopoulos, Steven G. Johnson, etc.

SPP的激发—相位匹配

• 激发SPP, 入射光波矢应该满足:

$$k_{\text{xinc}} = \beta_{\text{SPP}}$$
 (被称为 "相位匹配条件")

为什么呢? ——光子的横向动量守恒!

光子动量: $P = \hbar k$

约化普朗克常数: $\hbar=h/(2\pi)$

 $h=6.63 \times 10^{-34} \text{ J} \cdot \text{s}$

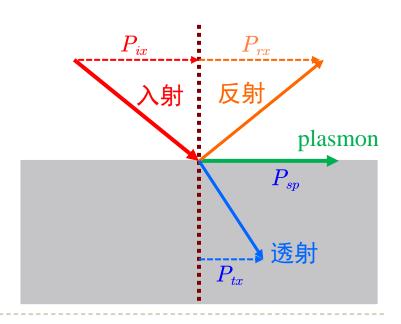
反射: $P_{ix} = P_{rx} \Rightarrow \hbar n_1 k_0 \sin \theta_i = \hbar n_1 k_0 \sin \theta_r$

 $\Rightarrow \sin \theta_i = \sin \theta_r$ 反射定律

折射: $P_{ix} = P_{tx} \Rightarrow \hbar n_1 k_0 \sin \theta_i = \hbar n_2 k_0 \sin \theta_t$

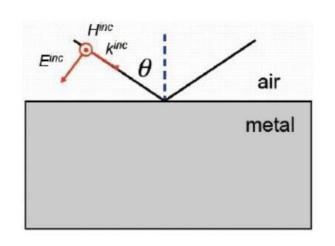
 $\Rightarrow n_1 \sin \theta_i = n_2 \sin \theta_t$ 折射定律

SPP: $P_{ix} = \hbar \beta$???



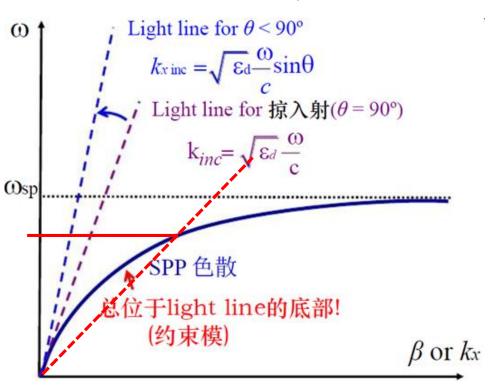
SPP的激发—相位匹配

$$\omega = rac{c}{\sqrt{arepsilon_{
m d}}\sin heta}k_x = rac{c}{n\sin heta}k_x$$



入射波矢的x分量:

$$\mathbf{k}_{xinc} = \mathbf{k}_{inc} \sin \theta = \sqrt{\varepsilon_d} \frac{\omega}{c} \sin \theta$$



- **同一频率下**, SPP波数总是大于介质中入射光的波数
- 没有交集的色散曲线 → **无**耦合进的光 和 **无**耦合出的表面等离激元
- 因此,必须采用某些"技巧"来增大 k_{xinc} 与 β_{spp} 匹配。

1.1 棱镜耦合—全反射

折射波可以表示为:

$$\boldsymbol{E}_{2} = \boldsymbol{E}_{20} \exp \left[\mathrm{i} (k_{2x} x + k_{2z} z) \right] e^{-\mathrm{i} \omega t}$$

x方向动量守恒: $k_{2x} = k_{1x} = k_1 \sin i_1$

$$k_{2z} = \sqrt{k_2^2 - k_{2x}^2} = \sqrt{k_1^2 \left(\frac{n_2}{n_1}\right)^2 - k_1^2 \sin^2 i_1}$$
,全反射角: $\sin i_c = \frac{n_2}{n_1}$

$$\Rightarrow$$
 k_{2z} $=$ $k_1\sqrt{\sin^2i_c-\sin^2i_1}$ $=$ $\frac{2\pi}{\lambda_1}\sqrt{\sin^2i_c-\sin^2i_1}$

当 $i_1 > i_c$,发生全内反射, k_{2z} 为纯虚数,令 $k_{2z} = i\kappa$

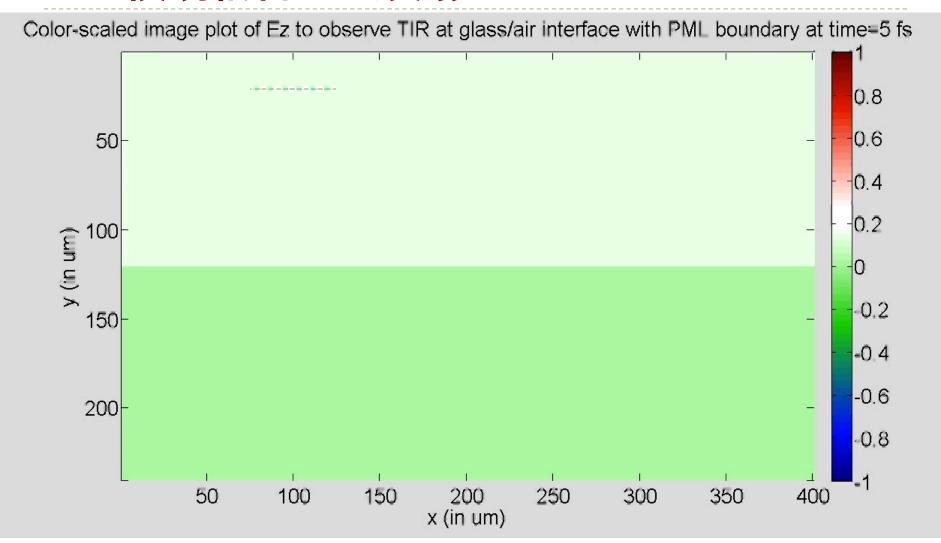
$$\sin i_c = \frac{n_2}{n_1}$$

$$oldsymbol{E}_2 = oldsymbol{E}_{20} \mathrm{e}^{\mathrm{i} \left(k_{2x} x + k_{2z} z
ight)} e^{-\mathrm{i}\,\omega t} = oldsymbol{E}_{20} \mathrm{e}^{-\kappa \mathfrak{z}} e^{\mathrm{i} \left(k_{2x} x - \omega t
ight)}$$

指数衰减

- 全反射情况下,入射波的能量是**穿透介质2内一定深度**后逐渐反射的
- 倏逝波的横向波数 k_x 依然保持不变!

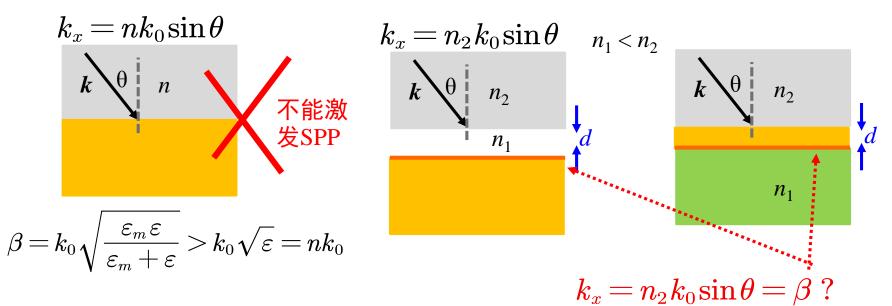
1.1 棱镜耦合—全反射



Prism coupling 12

1.1 棱镜耦合—全反射

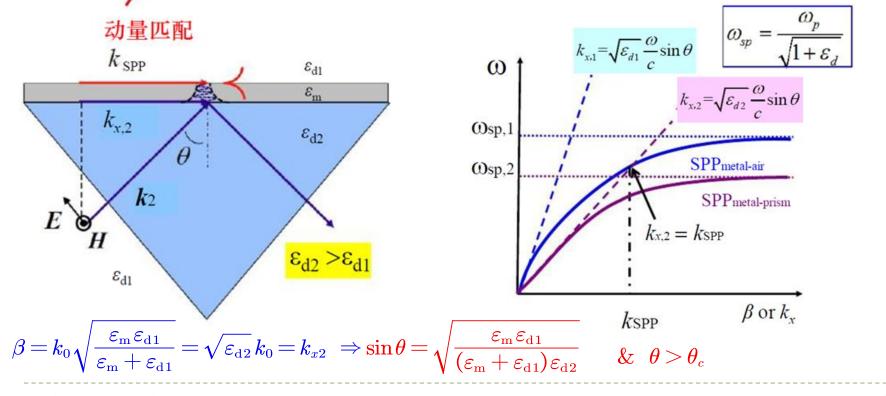
- ▶ 高折射率中光在 x 方向的波数: $k_x = nk_0 \sin\theta$
- ightharpoonup 对于确定的角度, k_x 正比于折射率
- ▶ 如果SPP的波数正好和 k_x 相等即可发生耦合,实现SPP激发
- ▶ SPP的波数大于介质中光的波数,如果是倏逝波呢?



d 很小, 倏逝波可以到达金属或穿越金属

1.1 棱镜耦合——动量守恒(波矢补偿)

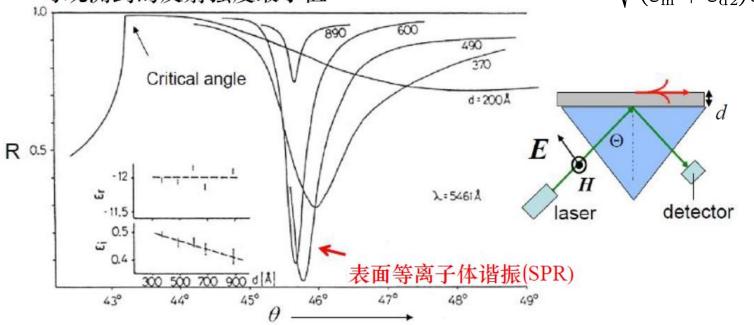
- 在棱镜中, 通过全内反射(TIR)产生倏逝波
- 倏逝波发生隧穿透过薄膜达到空气和金属界面
- 倏逝波的 k_x 与棱镜介质中光波的 k_x 一致!(动量守恒)



1.1 棱镜耦合

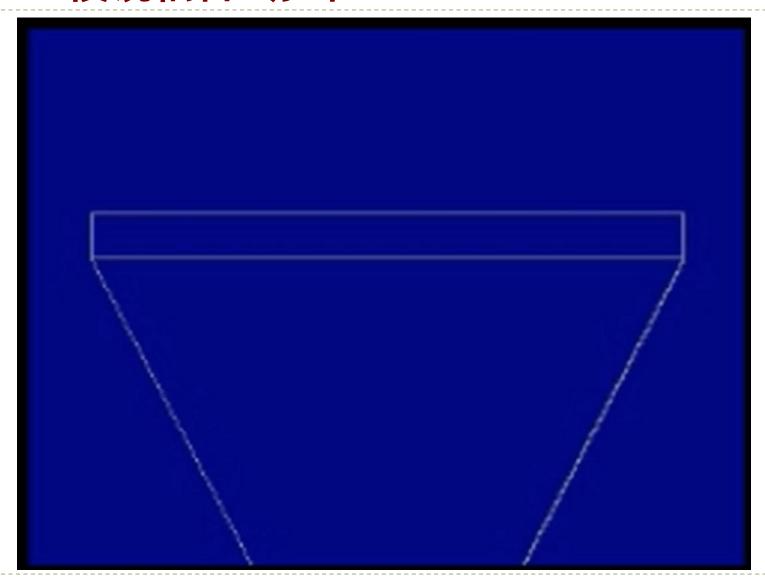
- SPP 激发时,能量从入射光转移到 SPP
 - →可观测到的反射强度最小值

$$\sin heta = \sqrt{rac{arepsilon_{
m m} arepsilon_{
m d2}}{(arepsilon_{
m m} + arepsilon_{
m d2}) arepsilon_{
m d1}}}$$

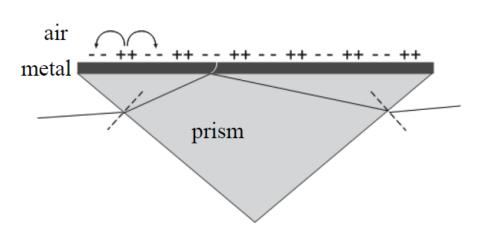


- •对薄膜厚度的依赖性: 存在完美耦合的最佳厚度
- •谐振宽度与SPP的阻尼有关
- •被激发的SPP是泄漏波:将辐射泄漏到棱镜中
- •最小值是由泄漏波和直接全内反射波干涉相消引起的

1.1 棱镜耦合-动画

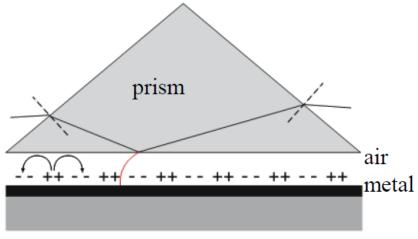


1.1 两种棱镜耦合结构



Kretschmann 结构

•需要在棱镜上蒸镀金属薄膜



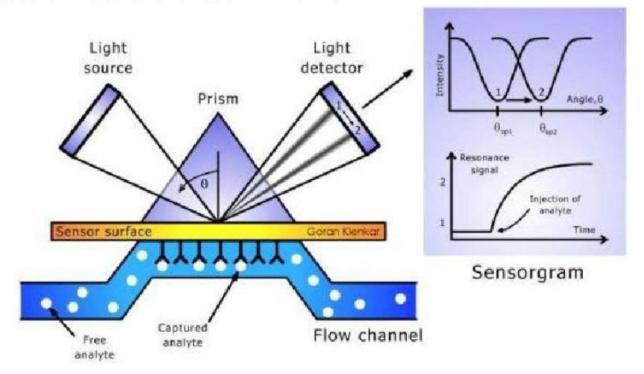
Otto 结构

- •避免零件与金属表面直接接触
- •空气间隙应控制得足够小

Prism coupling 17

SPR应用

用于监测生物分子:蛋白,配位体,DNA,等。



原理:

- SPR对表面敏感
- •抗体附着在金表面

•互补抗原(被分析物)与抗体结合→折射率n_d变化→SPR谷移动(监测信号)

 $\sin heta = \sqrt{rac{arepsilon_{
m m} arepsilon_{
m d}}{(arepsilon_{
m m} + arepsilon_{
m d}) arepsilon_{
m d} 2}}$

商业SPR仪器



Biacore3000

- •生物学检测
- •药物检测
- •食品及环境监测
- •蛋白质组学
- •临床诊断

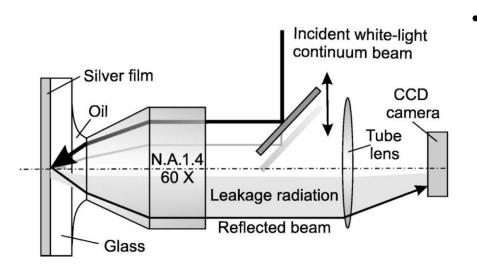


K-Mac SPRi Array korea



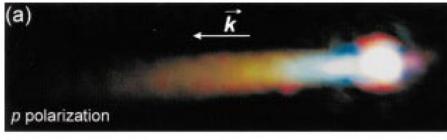
http://www.bionavis.com/technology/spr/

1.2 通过高度集中的光束激发



- · 是一种棱镜耦合的变化
 - —<mark>高数值孔径的油浸物镜</mark>代替棱镜

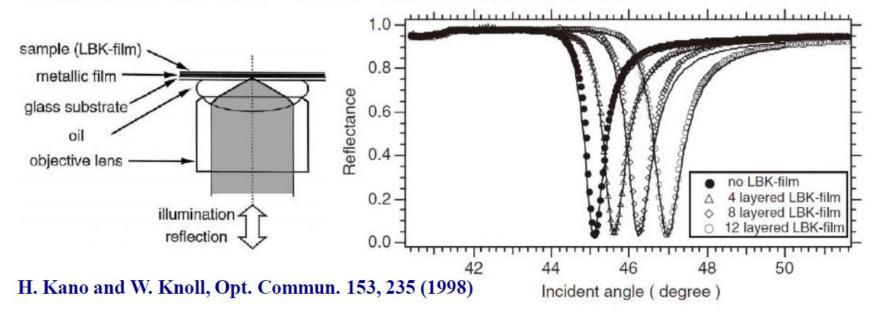
数值孔径
$$n$$
 $NA = n\sin\theta$





- 高数值孔径、θ大、离轴光线入射角大:全反射
- 离轴入口的光束 $\rightarrow \theta > \theta_c$ 时激发SPP
- 高度聚焦的光束 → 使局域SPP激发
- 泄漏辐射 → 观测激发的SPP

•Langmuir-Blodget-Kuhn (LBK) 功能分子转移薄膜厚度测量

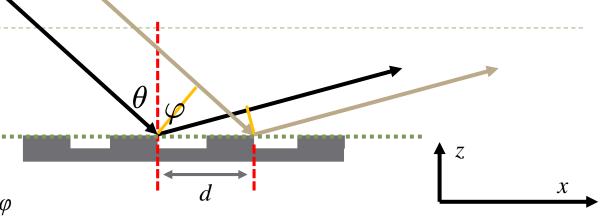


- ·原理: 薄膜厚度的变化→改变有效ε_d→SPR的移位
- ·耦合角度强烈依赖于LBK薄膜膜厚度
- •测量结果: 3.5nm, 7.3nm, 11.15nm的LBK厚度,
- · 几层LBK的检测是可行的!

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1.2 光栅耦合

▶ 光栅方程



入射角: θ , 衍射角: φ

光程差: $\Delta = d(\sin\theta - \sin\varphi)$ 如果衍射光在同一侧: $\Delta = d(\sin\theta + \sin\varphi)$

衍射极大条件: $d(\sin\theta \pm \sin\varphi) = m\lambda$ 光栅方程

x 方向波数: $k_{\text{inc},x} = k_{\text{inc}} \sin \theta$, $k_{m,x} = k_{\text{inc}} \sin \varphi$

$$\Rightarrow rac{d}{k_{ ext{inc}}}(k_{ ext{inc},x}\pm k_{m,x})\!=\!m\lambda$$

$$\Rightarrow k_{ ext{inc},x} \pm k_{m,x} = m rac{k_{ ext{inc}} \lambda}{d}, ~~ dots k_{ ext{inc}} = rac{2\pi}{\lambda}$$

$$\therefore k_{\text{inc},x} \pm k_{m,x} = mK$$
, 其中 $K = \frac{2\pi}{d}$

$$\pm k_{m,x} = k_{ ext{inc},x} - mK$$

把负号放入到 m 中,有:

$$\pm k_{m,x} = k_{\mathrm{inc},x} + mK$$
 需要的光栅方程形式

1.2 光栅耦合

- 光栅可以产生多个衍射级 (传播和消逝波)
- 第m级波矢满足:

$$\pm k_{m,x} = k_{\text{inc},x} + mK$$

$$K = \frac{2\pi}{d}$$

• 由于 $k_{\text{SPP}} > k_{\text{inc}}$, 只有倏逝级可能与SPP相位匹配:

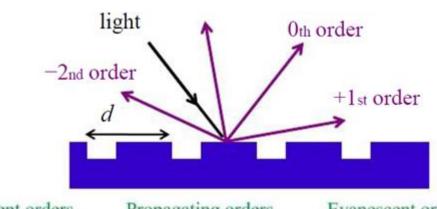
$$\pm k_{\text{SPP}} = k_{m,x} = k_{\text{inc},x} + mK$$

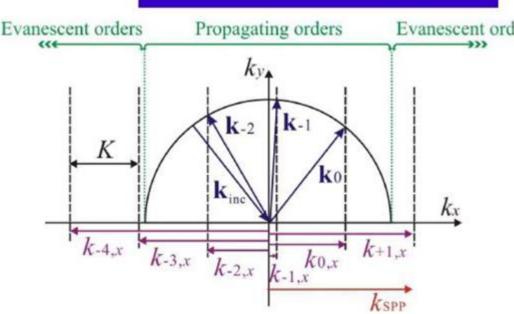


用此方法, SPPs 可以被激发!

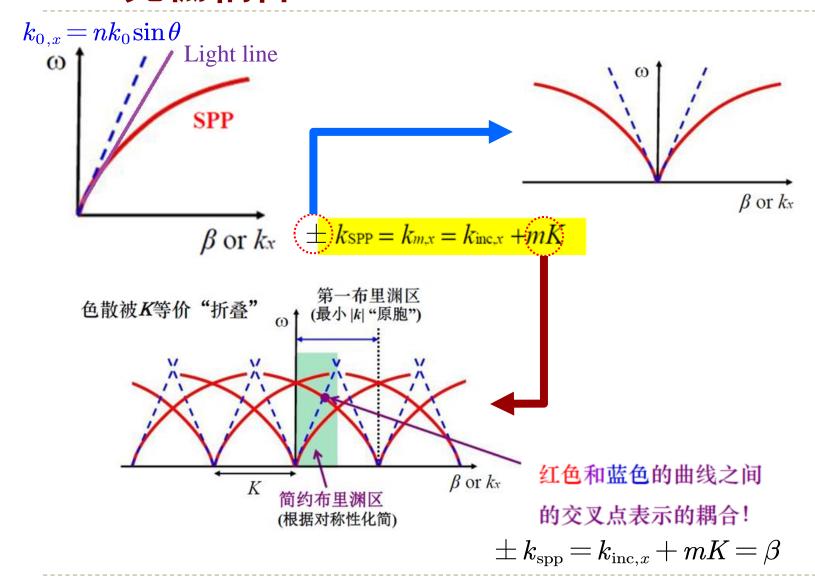
若 $k_{m,x} > k_{\text{inc}}$,

$$k_{m,z} = \sqrt{k_{ ext{inc}}^2 - k_{m,x}^2} = \mathrm{i}\sqrt{|k_{ ext{inc}}^2 - k_{m,x}^2|}$$
 倏逝波





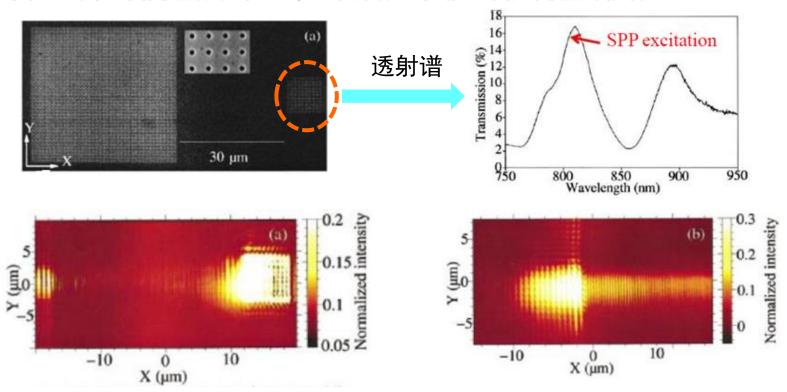
1.2 光栅耦合



SPP耦合成辐射光

相反的过程: SPP沿光栅表面传播也可以耦合成光从而产生辐射光

实验:用右侧光栅激发表面等离子体激元,被左侧大光栅解耦合

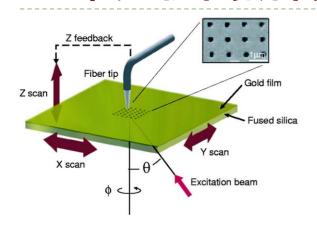


近场光学成像(λ = 800 nm)

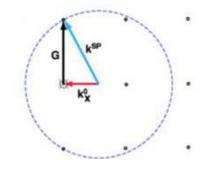
Devaux et al., APL 83, 4936 (2003)

二维光栅高阶衍射激发SPP

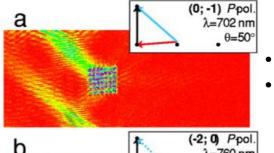
 $\lambda_{\rm spp}(\lambda_0)$

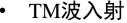


$$\mathbf{k}^{\mathrm{SP}} = \mathbf{k}_{x}^{0} \pm m\mathbf{G}_{x} \pm n\mathbf{G}_{y}$$

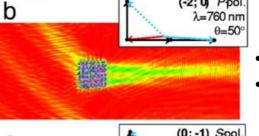


- 入射光波矢x分量 k_x 末端位于倒格点
- k_x 的起始点为圆心, k_{sp} 的长度为半径做圆
- 圆与倒格点相交的点满足激发SPP条件



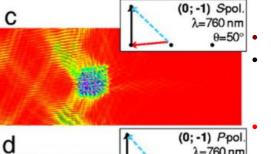


满足(0,-1)激发条件



TM波入射

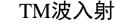
满足(-2,0)激发条件, 近似满足(0,-1)激发 条件



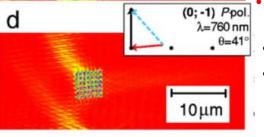
TE波入射

波矢满足(-2,0)激发条件,近似满足(0,-1)激 发条件

(-2,0)电磁模式不满足



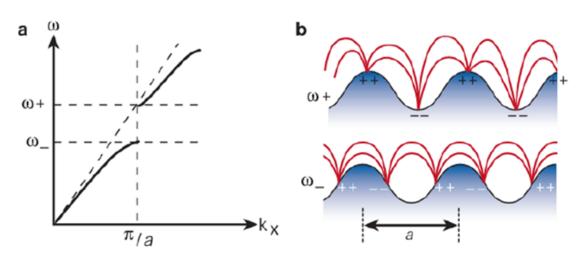
• 近似满足(0,-1)激 发条件



仿真结果

SPP带隙

- •当光栅很深→不再对表面产生小扰动
- ·发生SPP色散的显著变化
- •当d~λ_{SPP}/2: 散射导致形成SPP驻波→在布里渊区边缘形成SPP禁带 d 为光栅深度

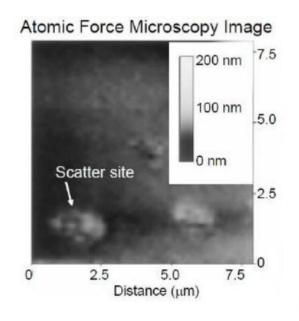


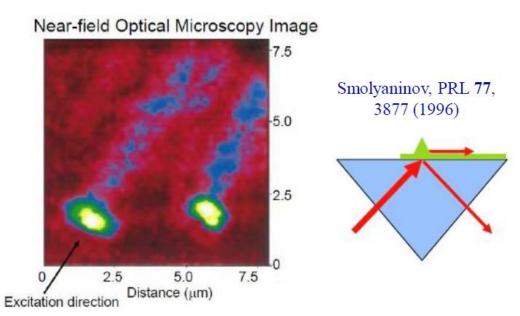
Barnes et al., Nature 424, 824 (2003).

类似于光子晶体,被称为"表面极化晶体"

Zayats and Smolyaninov, J. Opt. A: Pure Appl. Opt. 5, S16 (2003).

1.4 散射激发





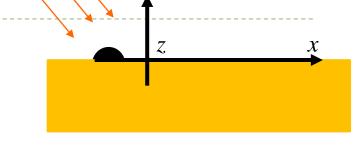
- •随机结构,如单孔,尖锐的边缘,颗粒和缺陷可以在局部激发SPP
- •发生在缺陷尺寸 $a << \lambda_0$
- •散射产生波矢为K的宽光谱(源自缺陷的空间傅立叶变换),可以找到耦合条件 $k_{SPP} = k_{inc.x} + K$ 的解。

表面缺陷是SPP转换为光传播的重要渠道,同时如果在SPP传播路径上有表面缺陷,也会导致SPP转换为辐射光辐射出去,造成SPP的损耗。

1.4 散射激发

考虑 x-z 平面上大小为 a 的颗粒(其中 $a << \lambda$), 光照后,位于z=0光场分布为(与颗粒相关):

$$E = E(x, 0)$$
 (2D处理,不考虑y方向)



对 E 做角谱展开:

$$E(x,0) = \frac{1}{\sqrt{2\pi}} \int A_0(k_x) e^{ik_x x} dk_x \quad A_0(k_x) = \frac{1}{\sqrt{2\pi}} \int E(x,0) e^{-ik_x x} dk_x$$
 其中: $k_x \leq \frac{2\pi}{a}$

位于 z 处的光场表示为:

$$E(x,0) = rac{1}{\sqrt{2\pi}} \int A(k_x, \mathbf{k}_z) e^{ik_x x} dk_x$$

z=0 平面光场受到颗粒调制,空间频 率上限为颗粒尺寸,具体频率成分需做 傅里叶分析

得到: $A(k_x, \frac{k_z}{k_z}) = A_0(k_x)e^{-ik_z z}$ 由霍姆霍兹方程: $\nabla^2 A + k^2 A = 0$

$$k_x^2 + k_z^2 = k^2$$
, if $k_x > k \Rightarrow k_z = i\kappa$ $A(k_x, \frac{k_z}{k_z}) = A_0(k_x)e^{-i\kappa z}$

空间频率小于波数

$$k_x = k_{inc,x} + \widehat{K} = \beta$$

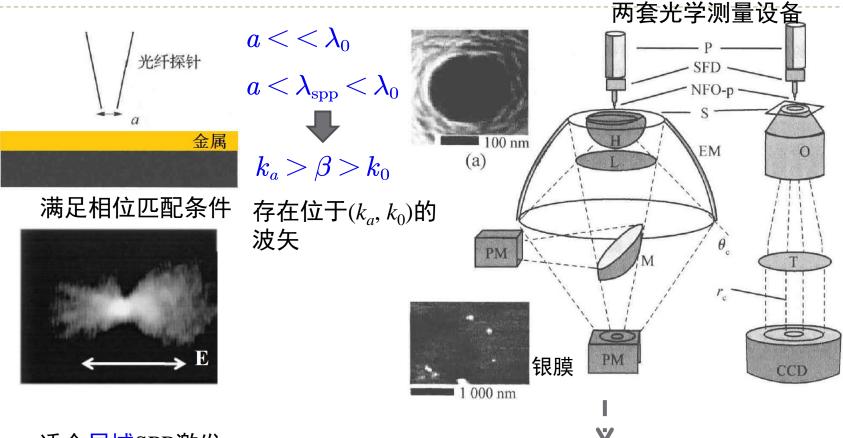
可以成立,与SPP匹配,可以激发SPP

不满足SPP匹配条件的,不能再金属-介质界面传播

1.5 近场激发

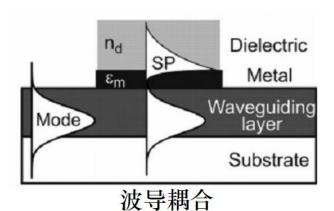
Hecht, Phys. Rev. Lett., 1996, 77, 1889

第11、12讲 近场光学与近场光学显微镜

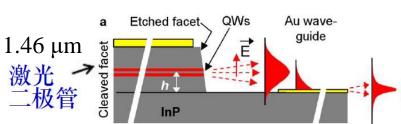


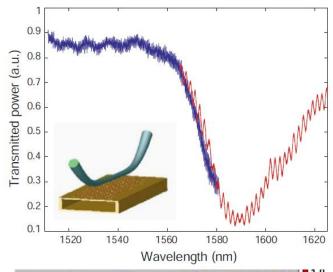
- 适合局域SPP激发
- 可以作为纳米级SPP点源
- 用于表征SPP上的表面粗糙度效应和具有高空间分辨率的单个表面缺陷的散射

1.6 其它激发(耦合)方式

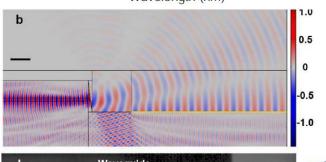


M 牙柄口 Homola, Chem. Rev. **108**, 462 (2008). (全反射)

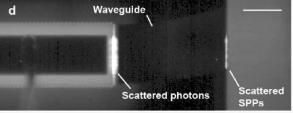




光纤锥体耦合 Maier et al., APL **84**, 3990 (2004).

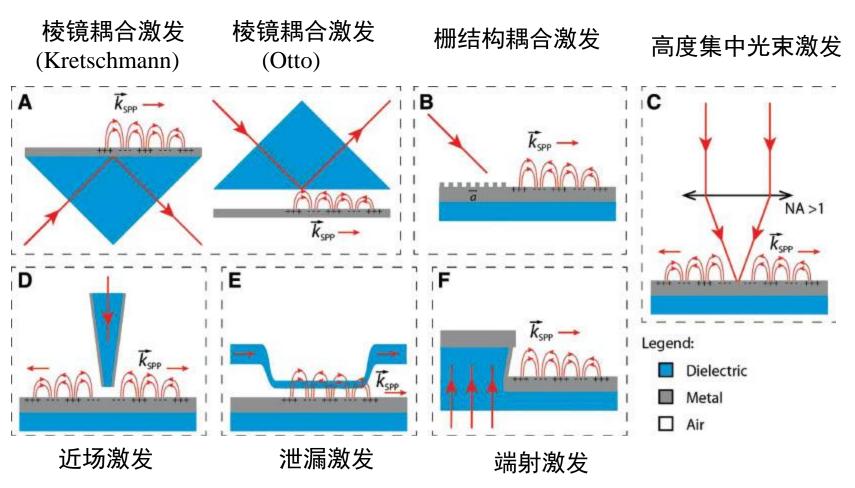


端射耦合



Kim et al., Opt. Express **18**, 10609 (2010).

激发方式小结



核心: 相位匹配 $k_{\text{inc},x} + K = \beta$ Fan Ye, et al. Nanophotonics 2014; 3(1-2): 33–49

激发方式小结

▶ 相位匹配是关键

$$k_x = k_{ ext{inc},x} + K = eta = k_0 \sqrt{rac{arepsilon_m arepsilon_d}{arepsilon_m + arepsilon_d}} > \sqrt{arepsilon_d} \, k_0$$

$$k_x = \beta > nk_0 = k$$

分量波数大小大于波数本身

$$k_z^2 = k^2 - k_x^2 < 0$$



$$k_z = \pm i \kappa$$

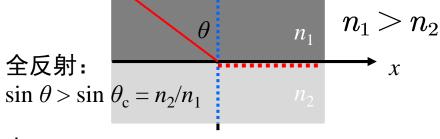
必然存在倏逝波

 $e^{\pm \kappa z}$

衰减 因子

- SPP本身也是一种倏逝波
- 倏逝波存在的条件: 传播常数大于对应介质中的波数

全反射在介质2中的倏逝波也满足



介质2中 传播常数:

$$k_{2x} = k_{1x} = n_1 k_0 \sin \theta > n_1 k_0 \sin \theta_c$$

$$k_{2x} > n_1 k_0 \sin \theta_c = n_2 k_0 = k_2$$

本讲内容

SPP的激发

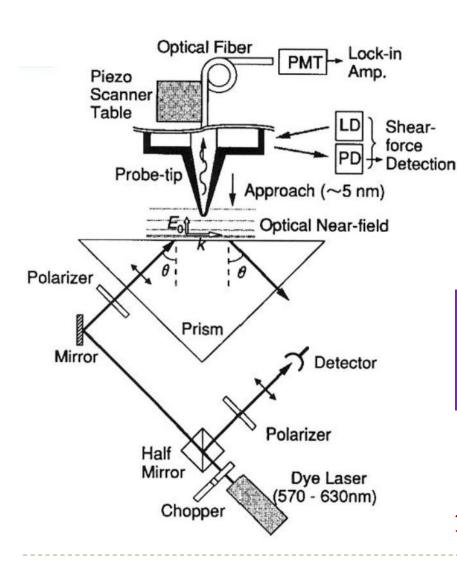
- ▶ 1.1 棱镜耦合
- ▶ 1.2 光栅耦合
- ▶ 1.3 通过高度集中的光束激发
- ▶ 1.4 散射激发
- ▶ 1.5 近场激发
- ▶ 1.6 其它耦合方法

2. SPP的表征

- ▶ 2.1 近场显微镜
- ▶ 2.2 泄漏辐射显微镜
- ▶ 2.3 荧光成像

Outline

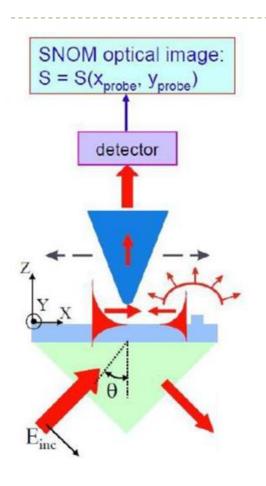
2.1 近场显微镜



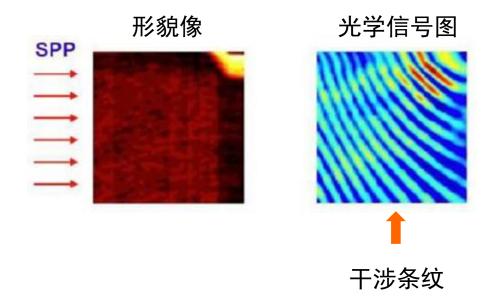
- · SPP波通过棱镜耦合产生的
- •通过扫描近场光学显微镜 (SNOM) 进行SPP波成像
- •将探针尖端插入"近场"
- •近场光学是必不可少的!

关键:光纤探针对金属/空气界面的 SPP空气一侧的倏逝波造成了扰动, 使局域在界面的SPP变为辐射波,被 探针收集。

第11、12讲 近场光学与近场光学显微镜

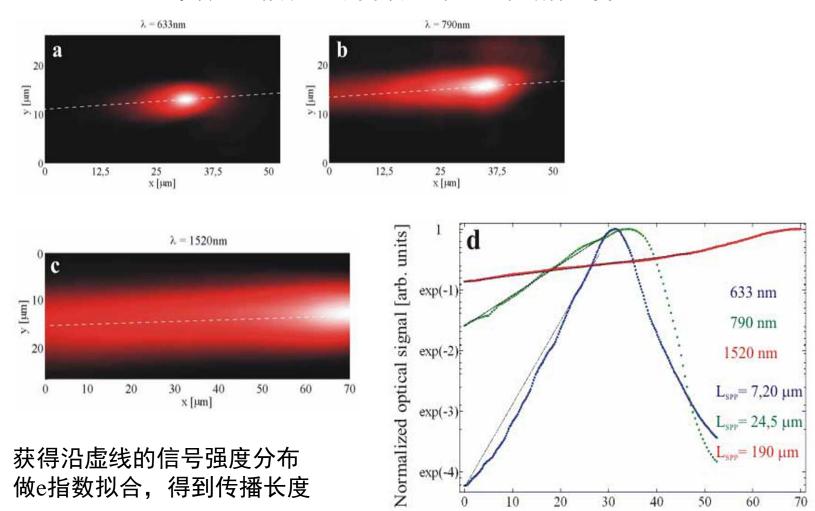


实例:由一个缺陷引起的SPP的散射

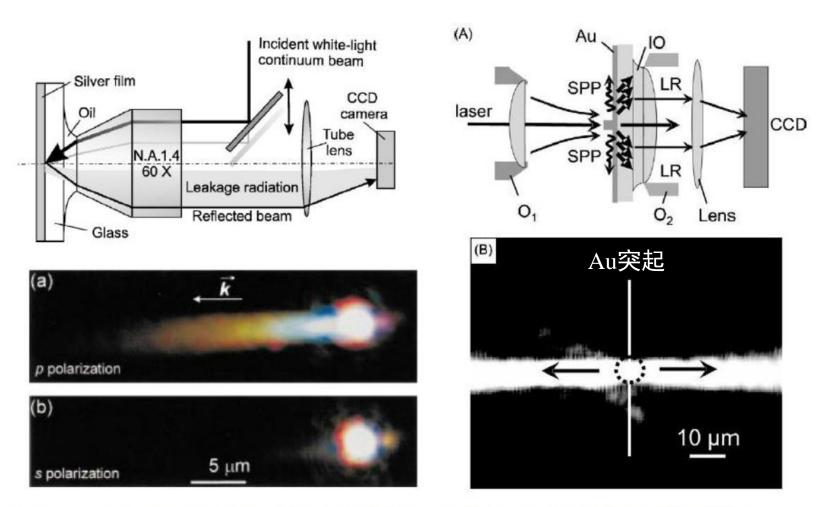


激发光波长为633 nm, p波 棱镜表面镀有45 nm的金属银

金薄膜: 直接决定不同波长的SPP的传播长度

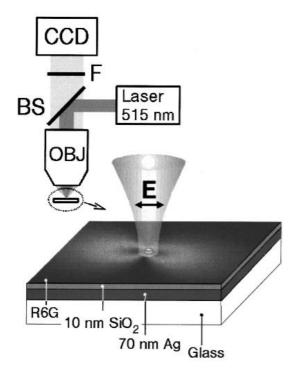


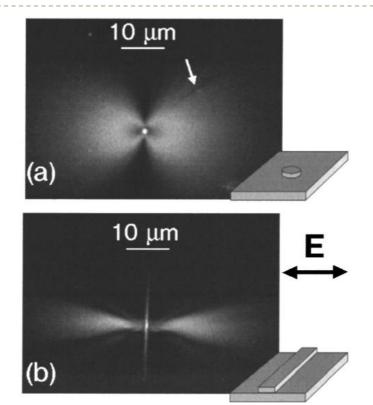
2.2 泄漏辐射显微镜



Further reading: Drezet et al., Materials Science and Engineering B 149, 220 (2008).

2.3 荧光成像





- 金属表面有一层荧光材料,如罗丹明6G
- 物镜将激发光聚焦在缺陷处,产生SPP
- SPP被荧光分子吸收,然后发出荧光,荧光被物镜收集并成像,从而显示SPP的分布
- •依赖放置在承载SPP的金属表面附近有机分子的荧光
- •由于分子漂白荧光图像必须在一个有限的时间(通常是几秒钟)内被记录下来
- •荧光强度一般不正比于局域SPP场强→不适合定量测量

小结

·SPP的激发

SPP不能通过平面上的光直接激发 了解不同耦合方法的原理和特点

棱镜耦合 通过高聚焦光的激发

光栅耦合 散射激发 近场激发 其他耦合耦合方案

·SPP的表征

成像方法

近场显微镜 泄漏辐射显微镜

荧光成像