多量子阱$GaAs/Al_xGa_{1-x}As$电极的瞬态光电流行为①

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由于半导体超晶格(量子阱)能带的量子化,使其具有许多完全不同于体材料的新特性.如激子寿命长、光吸收性能强、光生热载流子能量弛豫慢、载流子迁移率高等.这些特性都有利于提高光能的转移效率.因此,超晶格(量子阱)材料作为一种新型的光电极材料在光电化学能量转换研究中已引起人们广泛的注意和重视[1].

研究光照下的超晶格(量子阱)电极的电荷弛豫过程可以得到有关界面电荷转移、表面复合等动力学参数,进行分析这类新材料的光能转换动力学过程,了解其不同于一般体材料的一些新特性,为设计高效光电转换体系提供有用信息.而频率域分析的脉冲光瞬态光电流谱是研究半导体/溶液界面电荷转移、表面复合和电解池常数(RC)的有效技术和方法[2].本文利用Pade-Laplace变换方法分析和比较了晶格匹配型多量子阱$GaAs/Al_xGa_{1-x}As$电极在非水溶液中的瞬态光电流行为.

本文所研究的$CaAs/Al_xGa_{1-x}As$多量子阱电极(MQW)由分子束外延技术生长而成,其结构为:以n^+-GaAs(100)(掺杂浓度1×10^{18} cm^{-3})为衬底,依次生长200 nm n-GaAs缓冲层、2 000 nm n-$Al_xGa_{1-x}As$内垒(都是Si掺杂,浓度为$5\times10^{16}cm^{-3}$)、10周期10 nm/5 nm量子阱层(不掺杂)、最后为10 nm厚的GaAs保护层(不掺杂).势垒层Al含量x值通过低温光致发光谱测定为0.3.电解液为$9\times10^{-3}/1\times10^{-3}$mol·$dm^{-3}$ Fc/Fc^+——0.1 mol·dm^{-3} Bu_4NBF_4的乙腈溶液.以饱和甘汞电极为参比电极,4 cm^2 Pt片为辅助电极.电极电位由一直流电源控制.瞬态光电流由Nicolet 2090-2型数字存贮示波器记录.800 nm单色光脉冲由脉冲氙灯通过单色仪产生.脉冲宽度7 μs,单个脉冲能量为9 nJ·cm^{-2}.数据用自编的Pade-Laplace程序进行分析.

MQW电极的能级存在明显的量子化效应,表现为室温下的稳态电流谱中存在两个明显的结构峰,一个位于1.503 eV,另一个位于1.699 eV.它们分别对应于理论跃迁选律允许的($\Delta n=0$)两个重空穴H11及H22跃迁的激子峰.

MQW电极在不同电极电位下的瞬态光电流谱表示在图1中.从图中可以看到光电流衰减

① 本文1994-09-06收到,1994-09-24收到修改稿; 国家自然科学基金资助项目

曲线随着电极电位的负移而变化，主要表现为光电流衰减幅度减少，呈现出n型半导体光电流特性. 利用Pade-Laplace变换方法对瞬态光电流谱进行数据拟合可知光电流的衰减过程实际上是由快、慢两个过程组成. 图2表示了归一化的光电流与衰减时间的半对数关系，由图中拟合的曲线可看出光电流衰减曲线分为两个不同斜率的直线段，它们对应于光电流衰减的快、慢两个指数衰减过程，分别代表RC过程和表面复合过程.

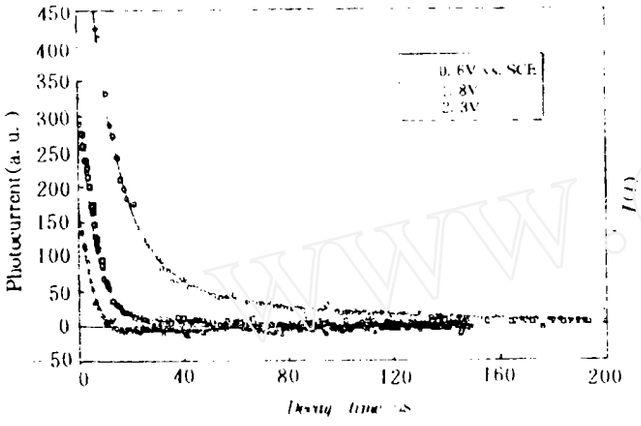

图1 MQW电极在Fc/Fc^+溶液中不同电极电位下的瞬态光电流谱

Fig. 1 The transient photocurrent spectra for MQW electrode in Fc/Fc^+ solution at the various electrode potentials

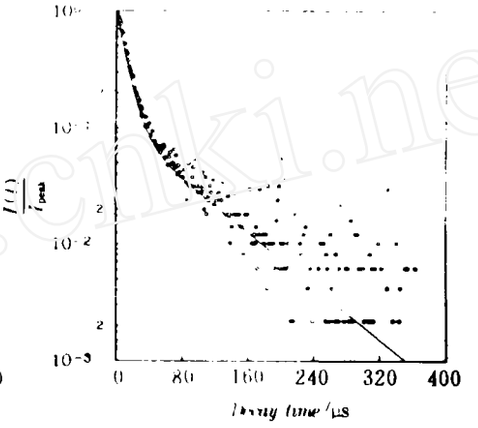

图2 MQW电极在电极电位为−0.6 V时的归一化光电流与衰减时间的半对数关系

Fig. 2 The semilogarithmic plot of normalized transient photocurrent vs decay time for MQW electrode at −0.6 V vs SCE

MQW半导体电极的瞬态光电流衰减曲线可用双指数方程来描述，即$I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$. 其中$A_1$，$A_2$，$\tau_1$，$\tau_2$分别为快、慢两过程的衰减幅度和寿命. 利用Laplace变换可求出光电流衰减的界面传递函数$Li(s)/Lg(s)$，从而进一步在频率域中计算出光电流衰减动力学参数——归一化稳态光电流和表面态寿命[3]. 为了比较，在相同实验条件下用同样方法还测量了GaAs电极光电流衰减动力学参数.

归一化稳态光电流为光电流衰减在频率域中频率为0时光电流I_s与少子收集系数G_0的比值，表示为I_s/G_0. 它表征光生载流子在稳态时参与界面电荷转移的比例. I_s/G_0与电极电位的关系如图3所示. 随电极电位从−2.3 V正移到0 V. 归一化稳态光电流逐渐增大. 这说明电极电位的正移使MQW电极的带弯增大，导致光生载流子有效的分离，本体及表面复合明显下降. 在相同电极电位下与GaAs电极相比，MQW电极的归一化稳态光电流明显大于GaAs电极. 这是由于MQW电极量子阱中的光生载流子具有较长的激子寿命，本体及表面复合小，参与界面电荷转移的载流子浓度增加，从而使I_s/G_0增加. 这说明MQW电极有利于提高光电转换效率.

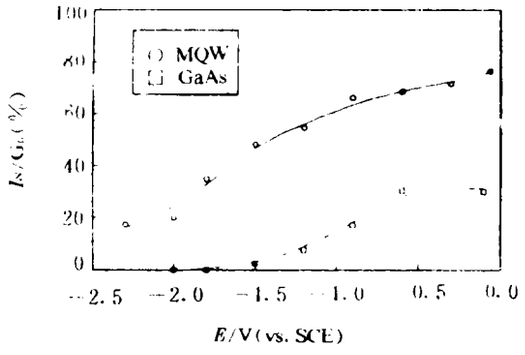

图3　归一化稳态光电流I_s/G_0与电极电位的关系

Fig. 3　Effects of electrode potentials on normalized steady-state photocurrent I_s/G_0

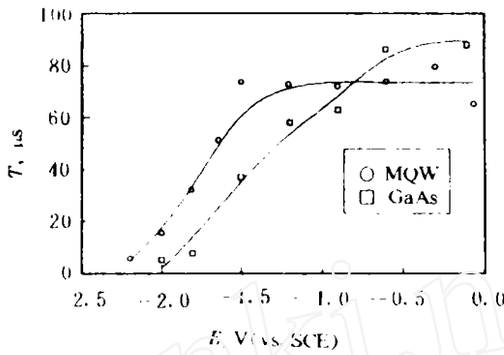

图4　表面态寿命T_s与电极电位的关系

Fig. 4　Influences of electrode potentials on the surface state lifetime T_s

表面态寿命T_s是表面态所参与反应的反应速率之和的倒数，它反映了表面复合的快慢程度. T_s越大，表面复合越慢. 图4表示了T_s与电极电位的关系. 在电极电位较负时，MQW电极的表面态寿命T_s大于GaAs电极. 说明MQW电极的表面复合速度较慢. 随电极电位的正移，MQW和GaAs电极的T_s都不断增加，MQW电极的T_s很快达到恒定值(−1.5 V时)，而GaAs电极的T_s在−0.7 V时才趋向恒定值. 在较正电位下，MQW电极的T_s小于GaAs. 这是因为所研究的MQW电极可能存在异质结的界面态，这种界面态是可在MQW生长过程中避免的. MQW电极的表面复合速度慢，表明其电性能优于GaAs电极.

Transient Photocurrent Behavior of Multiple Quantum Well GaAs/$Al_xGa_{1-x}As$ Electrode

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Abstract　Transient photocurrents induced by short light pulses at lattice-matched multiple quantum well(MQW) GaAs/$Al_{0.3}Ga_{0.7}As$ electrodes were studied in the 1×10^{-2}mol·dm^{-3}ferrocene ($[Fc^0]/[Fc)^+]=9/1$)—0.1 mol·dm^{-3}tetrabutylammonium tetrafluoroborate acetonitrile solution in order to examine the relaxation photoprocesses and to evaluate kinetic parameters of superlattice

electrodes.

GaAs/$Al_{0.3}Ga_{0.7}As$ MQW electrode consisting of 10 periods with each of GaAs well (5.3 nm) and $Al_{0.3}Ga_{0.7}As$ barrier (10 nm) showed two pronounced and well-resolved peak structures located at 1.503 eV and 1.699 eV in the photocurrent spectrum, corresponding to the theoretical allowed excitonic transitions ($\Delta n = 0$) for heavy holes (H11, H22) in the quantum well respectively.

Transient photocurrent spectra were measured by a monochromatic light pulse with 7 μs pulse width and 9 nJ · cm^{-2} of energy at $\lambda = 800$ nm produced by a pulsed xenon lamp via a monochromator, and analyzed by Pade-Laplace transform method. Photocurrent transients were characterized by a rapid decays following by a slow exponent at the electrode potential varying from −2.3 V to 0 V vs SCE, and exhibited typical I-V behaviours of n-type semiconductor. Dual exponential transient photocurrent decay were demonstrated by the two segments with different slope in the relations of normalized logarithm of photocurrent response and decay time, representing two processes-RC (fast) and surface recombination (slow). By fitting the transient decay to the dual exponent function of the form: $I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$, where t is the decay time, A_1, A_2 and τ_1, τ_2 correspond to the amplitudes and time constants of the fast and slow decays respectively. The kinetic parameters such as the normalized steady state photocurrent (I_s/G_0) and surface state lifetime (T_s) were determined in frequency domain. Both of the I_s/G_0 defined as the relative ratio of photogenerated carrier transferred from the electrode to electrolyte and the T_s reflected the rate of the surface recombination increased with the positive shifts of electrode potential, due to fast separation of photogenerated electron-hole pairs and slow surface recombination resulted by the larger band bending created at more positive potential. Comparison with GaAs electrode, significantly larger I_s/G_0 were obtained in the potential range of −2.3 V to 0 V vs SCE, and longer T_s at more negative electrode potential for MQW electrode, indicating that the longer lifetime of exciton presented in the MQW electrode leads to less bulk and surface recombination and higher concentration of photogenerated carriers at the interface. The increase of light to electric conversion efficiencies is, therefore, reasonably available in the MQW electrode systems.

Key words Superlattice(quantum well), Multiple quantum well, Transient photocurrent

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