$GaAs/Al_xGa_{1-x}As$ 量子阱电极/非水溶液界 面 性 能 的 研 究

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摘要　用阻抗谱研究了晶格匹配型单、多量子阱 $GaAs/Al_xGa_{1-x}As$ 电极在二茂铁乙腈溶液中的界面性能. 得到了空间电荷层电容及表面态电容与电极电位的依频关系. 空间电荷电容与量子阱电极的结构有关，而表面态电容则决定于电极的表面性质如表面氧化层及二茂铁的吸附. 分析和讨论了表面态的能级，密度的分布，来源和作用.

关键词　量子阱电极，阻抗谱，表面态

A Study on the Interfacial Behaviours of GaAs/Al$_x$Ga$_{1-x}$As Quantum Well Electrode/Nonaqueous Electrolyte[①]

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The quantum well semiconductors (QWs) as a new kind of photoelectrodes have drawn much attention to the study of photoelectrochemical energy conversion. Due to the energy quantization of semiconductors with low dimensional structure, the higher energy conversion efficiency approaching to $40\% \sim 50\%$ is theoretically possible in QWs incorporated solar cells systems[1]. In order to understanad the photoelectrochemical behaviours of QWs electrodes, we have studied the characteristics of QWs/solution interface which play important roles in the dynamics and thermodynamics of photoelectrochemical energy conversion processes[2,3], such as the nature of surface states produced by the unpaired dangling bonds, defects of crystal structure, oxidations of surface and the adsorptions of specific chemical species (ions, molecules), these influences considerably the interface energetics and interfacial charge transfer processes. In this communication, we report the interfacial behaviours of lattice-matched single (SQW) and multiple quantum well (MQW) electrodes in ferrocene-acetonitrile solution by impedance measurements.

The lattice-matched quantum well electrodes consisting of GaAs well and Al$_x$Ga$_{1-x}$As barrier were grown by the molecular beam epitaxy (MBE) on n^+-doped GaAs(100) substrates ($N_d = 1 \times 10^{18}$ cm^{-3}) coated with a 0. 2 μm n-GaAs epilayer and 2 μm n-Al$_x$Ga$_{1-x}$As epilayer (both Si doped, 5×10^{16} cm^{-3}) sequentially prior to the growth of QWs. Two kinds of electrodes SQW and MQW were studied, SQW with a single GaAs well(thickness of 5 nm), Al$_x$Ga$_{1-x}$As outer barrier(10 nm), and GaAs capped layer(10 nm) and MQWcontaining 10 periods of 5 nm thick GaAs well and 10 nm thick Al$_x$Ga$_{1-x}$As barrier, finally 10 nm GaAs capped layer, were mounted as electrodes in a conventional three-electrodes cell using a Pt foil(4 cm^2) as counter electrode and the standard calomel electrode

（SCE） as the reference electrode. The aluminum fraction x which was determined by photoluminescence （PL） at 10 K was 0. 3. The impedance measurements were carried out in the acetonitrile solutiion containing 1×10^{-2} mol · dm⁻³ ferrocene[Fc]/[Fc⁺]＝9/1 and 0. 1 mol · dm⁻³ tetrabutylammonium fluoroborate （Bu₄NBF₄）, under dark, at the potential range of — 1. 5 to 0. 5 V by conventional lock-in technique with frequencies from 5 Hz to 100 kHz. Data were collected with M378 software and analysed with compiled routine of optimization.

A typical impedance spectra of QWs electrodes measured at — 0. 5 V are shown in Fig. 1. Two semicircles were exhibited in the spectra of SQW and MQW electrodes indicating that the processes of interfacial relaxation of QWs electrodes consist of two processes with different time constants. The centers of semicircles located at the real axis of corresponding diagrams. The real part of impedance decreased with the increase of frequency. The intercepts of the real part of impedance in the high frequency domain were about 1 500 Ω equivalent to the series resistance of QWs/nonaqueous solution system. Based on the impedance spectra, two equivalent electrical circuits （Ⅰ） and （Ⅱ） describing the behaviours of QWs/solution interface are shown in Fig. 1, where R_{so} is the series resistance, C_{sc}, R_{sc} and C_{ss}, R_{ss} represent the capacitance and resistance of the space charge layer （SPL） and surface states respectively. Analysis of impedance data by equivalent circuits （Ⅰ） and （Ⅱ） has proved that better fitting results with reasonable calculated values of capacitance and resistance elements were obtained with equivalent circuit （Ⅰ） which usually represents the case of surface recombination at semiconductor/solution interface.
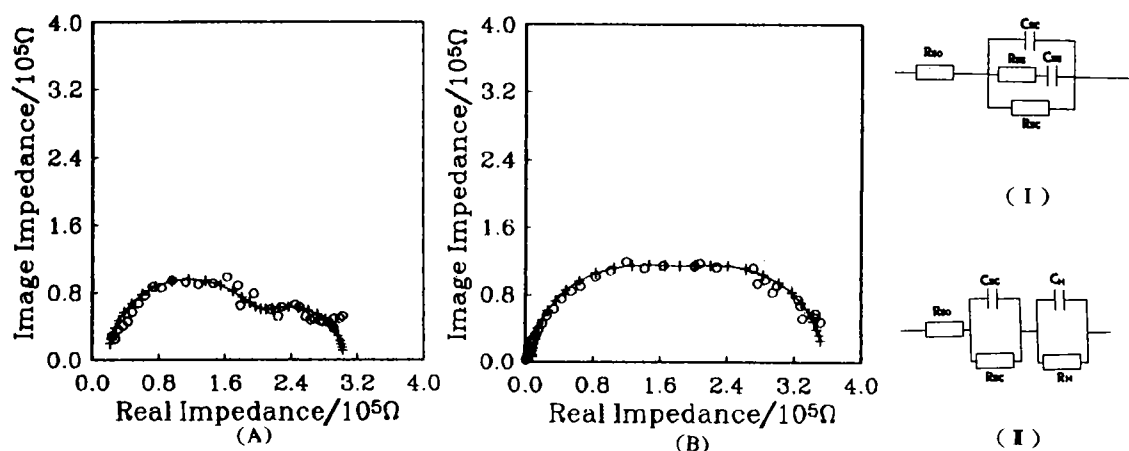

Fig. 1　The impedance spectra and equivalent circuits for quantum well electrodes at — 0. 5 V in ferrocene-ace-
tonitrile solution （A)SQW （B)MQW

（Ⅰ)（Ⅱ):equivalent circuits used to model quantum well electrode interface. In each case, R_{su}, R_{sc}, R_{ss}, R_H are the series, space charge layer, surface state and Helmholtz layer resistance, respectively. C_{sc}, C_{ss}, C_H are the space charge layer, surface state and Helmholtz layer capacitance.

Fig. 2 shows C_{sc} and C_{ss} as a function of electrode potential. The capacitance of SPL, C_{sc}, decreased as positive shifts of electode potential for both SQW and MQW electrodes due to increasing the width of SPL by larger band bending created at more positive potential. The larger of C_{sc} for MQW electrode compared to that fo SQW electrode is probably attributed to the higher heterojunction capacitance produced by the MQW within the·SPL and the uncompletely depleted region caused by the different doping concentration between the wells and barriers[4]. There are similarity in the magnitude and potential dependence for the capacitance of surface states, C_{ss} between SQW and MQW electrodes. Gauss distributions of C_{ss} were present at the potential range of -0.5 to 0.5 V with peak maximums located at 0 V. When potential negatively shifted, C_{ss} increased quickly and approached to another maximums at potential negative than -1.0 V. These results imply that two kinds of surface states existed in QWs electrodes/Fc solution interface. One positioned at 0 V and another at -1.25 V for SQW and -1.40 V for MQW electrode.
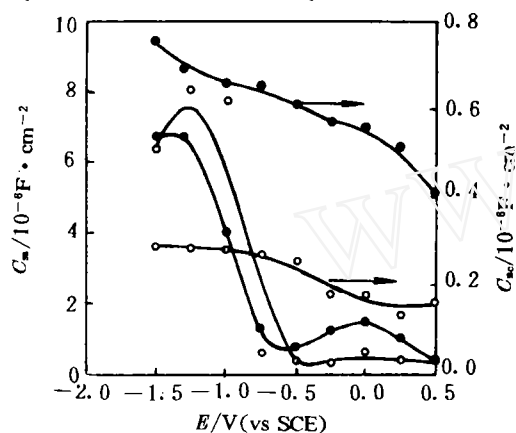
Fig. 2　Effects of electrode potential on the capacitance of space charge layer and surface states for quantum well electrodes. ○:SQW ● : MQW
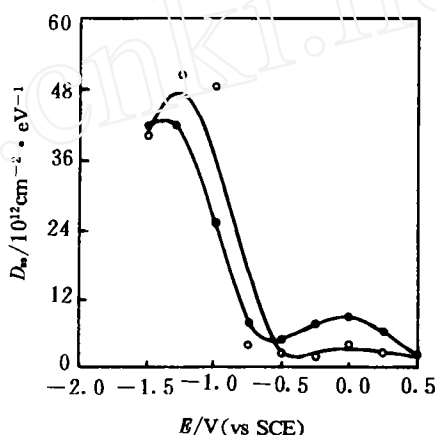
Fig. 3　The distributions of surface states density for quantum well electrodes. ○:SQW ● : MQW

The potential dependence of C_{ss} can be used to analyse the distribution of surface states density by following equation[1]:

$$D_{ss}=dN_{ss}/dE_{(1/q)}(dQ(E)/d1)=C_{ss}/q \quad (1')$$

(1)

where D_{ss}, N_{ss} and q denoted as the distrirution of surface states density, surface states density and electron charge respectively. The calculated D_{ss} as a function of the electrode potential was plotted in Fig. 3. The wider distributions of surface states density were observed for both SQW and MQW electrodes in Fc/Fc$^+$ acetonitrile solution demonstrating that the distribution of surface state density does not follow the Fermi-Dirac distribution. The surface states density N_{ss} can be obtained by integrating with the electrode potential. The calculated data of D_{ss} and N_{ss} for both QWs electrodes were collected in Table 1. From the Table, we observe that there are almost same magnitude of surface

states density for SQW and MQW electrodes at corresponding potentials revealing that the surface states are related directly to the interface rather than the structure of the QWs electrodes. In order to analyse the origins of surface states, the same experiements were performed in the benzoquinone/hydroquinone (BQ/HQ) solution and showed that only surface states located at -1.25 V (SQW) and -1.40 V (MQW) were observed in QWs electrodes/BQ/HQ solution interface suggesting that surface states at -1.25 V (SQW) and -1.40 V (MQW) are associated essentially with the surface natures of QWs electrodes, such as defects or oxidations of surface (QWs electrodes with 3 nm thick oxidized layer have been detected by Auger Electron Spectrum and Ion Sprayed Technique), while the surface states at 0 V which disappeared in BQ/HQ solution are contributed by the adsorption of Fc.

The surface states can also alter the distribution of electrode potential of the interface. The equation(2) was used to calculated the potential ratio fo the SPL to the Helmholtz layer[5].

$$\Delta V_{sc}/\Delta V_H = C_H/(q^2 D_{es})　　(2)$$

Where the ΔV_{sc} and ΔV_H are the potential drop across the SPL and the Helmholtz layer respectively. C_H is capacitance of the Helmholtz layer, useually about 20 μF/cm^2 [5]. Using the data given in Table 1, $\Delta V_{sc}/\Delta V_H$ is calculated to be 2.5~3, i.e. 25%~30% of electrode potential is across the Helmholtz layer. The remarkable effects of surface states on the interfacial behaviours of QWs electrode/solution interface are, therefore, comfirmed.

Tab. 1　The calculated date of D_{ss} and N_{ss} of the lattice-matched GaAs/Al$_x$Ga$_{1-x}$As quantum well electrodes.

	E_{ss}/V vs SCE	D_{ss}max/10^{13} cm^{-2} eV^{-1}	N_{ss}/10^{13} cm^{-2}
SQW	0	0.40	0.10
	-1.25	5.00	5.80
MQW	0	0.89	0.42
	-1.40	4.20	4.60

Key words　Quantum well electrodes, Impedance spectra, Surface states

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