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Strong Influence of the Humidity on the Electrical Properties of InGaAs Surface Quantum Dots

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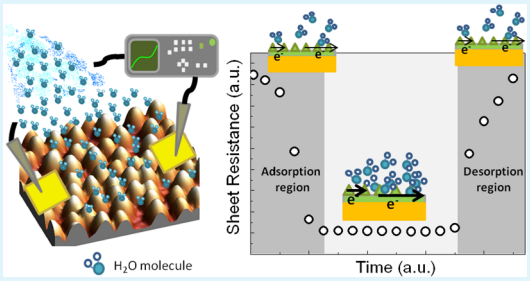
ABSTRACT: The impact of the environment on the electrical properties of uncapped $In_{0.5}Ga_{0.5}As$ nanostructures is studied as a function of different atmospheres for sensing applications. Electrical response from surface quantum dots (QD) shows a strong dependence on the atmosphere, in contrast to the response of 2D nanostructures. The sheet resistance drops by 99% from vacuum to air, and decreases more than one order of magnitude when relative humidity changes from 0 to 70%. The adsorption of water molecules onto the QD surface improves the conductivity likely by reducing the density of surface states acting as carrier traps, which enhances electron transport.



KEYWORDS: *InGaAs, quantum dots, humidity, adsorption, sensors, surface states*

In the last few years, the impact of the environment on life is of growing importance. Different issues including humidity and atmospheric pollution are subjects of intense research, not only to understand natural phenomena, but also to monitor and control the atmosphere quality.[1] Recently, many materials based on semiconductor technology such as porous silicon,[2] colloidal II−VI quantum dots (QDs),[3,4] ZnO nanostructures,[5] carbon QDs,[6] graphene[7] and III−V compounds[8−10] have been proposed for the development of environmental sensors. The last ones show many advantages over others in, for example, their high-speed operation, wide-range wavelength tuning via bandgap engineering and high mature technology. Among the various morphologies, 3-dimensional (3D) nanostructures deliver superior optical and electrical properties. Generally, III−V semiconductor QDs are intensively studied due to their unique features and great potential for optoelectronic applications. In particular, self-assembled InGaAs QDs embedded into wider bandgap materials are extensively investigated for the development of devices working in the range of telecommunication wavelengths (1.3-1.55μm). However, in the last decades, photoluminescence (PL) from InGaAs surface quantum dots (SQDs) has been observed even at room temperature (RT).[11] Furthermore, it has been shown that the optical properties of such uncapped QD layer strongly depend on the coupling between surface and confined states.[12−15] More recently, a strong influence of the external conditions in the optical emission of SQDs has been reported. PL intensity is maintained in water-vapor-containing atmospheres, whereas it decreases in dry environments and quenches under vacuum.[16] Many factors including the polar character, the shape, the structure and the weight of the molecules in the surroundings have been suggested to be responsible for similar effects.[17,18]

However, no much work is found in the current literature studying the impact of the external conditions on the electrical properties of SQDs. A significant sensitivity of the electrical response to the atmosphere would be an important step forward towards device applications.

In this letter, we study the influence of the environment on the electrical response of uncapped InGaAs nanostructures. We report an electrical analysis for such systems in several atmospheres. Indeed, we show a strong dependence of the SQDs conductivity on the environmental conditions and furthermore, we propose a high sensitive humidity sensor based on InGaAs SQDs.

To demonstrate the advantages of SQDs for the development of sensing device applications, we compare the electrical properties of 3 samples with different surface composition: a reference sample which corresponds to a 1.5μm GaAs thick layer (sample 1), a 2-dimensional (2D) $In_{0.5}Ga_{0.5}As$ surface quantum well (SQW) layer (sample 2) and a 3-dimensional (3D) $In_{0.5}Ga_{0.5}As$ SQDs layer (sample 3).

The samples were grown by solid-source molecular beam epitaxy (MBE) on a Si-doped GaAs (100) substrate. For all the structures, after oxide desorption, a 1.5μm GaAs buffer layer was grown at 590°C and 1ML/s. Following the GaAs buffer, the substrate is cooled down in the case of sample 1. In the case of samples 2 and 3 an $In_{0.5}Ga_{0.5}As$ SQW and a SQDs layer were grown, respectively, using low temperature (430°C) and slow growth rate (0.07ML/s). Before substrate cooling, the temperature was rapidly dropped to 330°C and then raised again to 430°C within 3 min. The amount of InGaAs deposited was 2.8 ML (1ML = 0.303 nm) for SQW (below the critical thickness for QD formation of 4.4ML) and 6ML for SQDs. The growth was monitored by *in-situ* reflection high-energy

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electron diffraction (RHEED) and the QD layer was formed by self-organized Stranski-Krastanov method.

Structural and electrical characterization was performed by using an Atomic force microscope (AFM) in tapping mode and a semiconductor parameter analyzer (HP4145), respectively. Regarding the current-voltage (I–V) measurements, we used two 150 μm-side square metal contacts of Ti/Au (10/130 nm) separated by 70μm. These contacts were not annealed to avoid the possible creation of a conduction channel below the wetting and SQDs layer. Several electrical measurements were performed in different external conditions.

A comparison of the sheet resistance (SR) of the 3 investigated samples measured under vacuum and air atmosphere is shown in Figure 1. The inset in each graph corresponds to a (0.5μm × 0.5μm) AFM image of the corresponding surface structure. Sample 1 and sample 2 present a mostly flat surface, with an average roughness of 0.29 and 0.30 nm, respectively. On the other hand, sample 3 exhibits 3D features. These QDs present a narrow size distribution and a high surface density ($7.1 \cdot 10^{10}$cm^{-2}), and they have an average height and base length of 6.7 ± 0.2 nm and 34 ± 1 nm, respectively (inset of Figure 2c). Figure 1 also shows the sheet resistance variation as a function of the applied bias under vacuum and air conditions. Despite the fact that all samples show an electrical dependence on the external conditions, the surface morphology seems to be an important factor to the surface sensitivity. As can be appreciated in Figure 1a and Figure 1b, sample 1 and sample 2 exhibit a maximum SR reduction of 31 and 20% from their value under vacuum to their response in air, respectively. Nevertheless, we found a stronger dependence (99%) on sample 3 (InGaAs SQDs), as it is plotted in Figure 2c. The SR of this sample under vacuum is ∼3 and ∼2 times larger than that of samples 1 and 2, respectively. This could be likely related to the presence of a large number of surface states acting as traps for carriers, as well as to the presence of energy barriers for the electron motion through the wetting layer-QD system. Meanwhile, when the external conditions are changed from vacuum to air, the SR of this SQD sample significantly decreases up to two orders of magnitude, leading to a strong increase of the surface conductivity. This behavior could be directly linked with the moisture in the surrounding. In fact, one of the main components of air is water vapor. Thus, the presence of a high density of water molecules in the atmosphere makes more likely their adsorption onto the surface, which would lead to a reduction of the SR, and therefore to an increase in the surface conductivity. This result demonstrates that the sensitivity of the surface to the ambient is not only due to the material itself (InGaAs) but also due to the particular structure of the QDs. In particular, the high volume to surface ratio of the SQD greatly improves the responsiveness to the atmosphere, making InGaAs SQDs a very suitable system with an exceptional performance for sensing applications.

To study the sensitivity of the sample to the surrounding conditions, our first experiment consists of a rough evaluation of the electrical response of the sample to the human breath. In Figure 2, we show several cycles of the sheet resistance of sample 3 measured applying a constant voltage of −2 V between contacts. This resistance was measured while exhaling air on the surface. It can be clearly recognized that the sheet resistance instantaneously decreases when the exhalation starts, and its value is maintained during the breathing time (10 s). Once the exhalation stops, the SR increases again recovering its

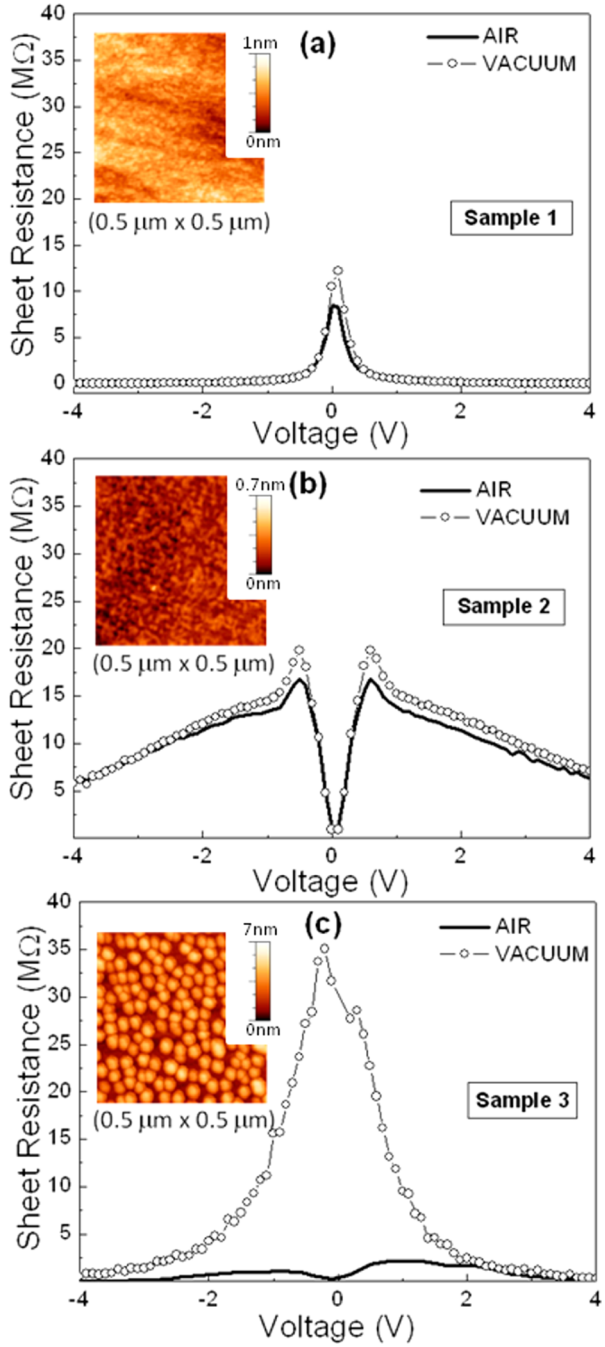

Figure 1. Electrical response of (a) the reference GaAs sample, (b) a sample containing a single SQW, and (c) a sample containing a single SQDs layer under vacuum and air atmosphere. The SR of 2D nanostructures does not suffer significant changes in a wide voltage range by varying the environment. The SR of SQDs is significantly increased under vacuum. The insets show (0.5 × 0.5μm^2) AFM images. Sample 1 and 2 have a smooth surface (average roughness of 0.29 and 0.30 nm, respectively) and sample 3 presents QDs with 6.7 ± 0.2 nm height and 34 ± 1 nm diameter.

initial value. Similar effects in several inorganic materials have been reported by Han et al. in 2012.[19] Although human breath is composed by several components such as nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), very small fractions of nitric oxide (NO), carbon monoxide (CO), and some volatile organic compounds,[20,21] the one that overwhelms all the rest is the high concentration of moisture.[19] Indeed, most of the

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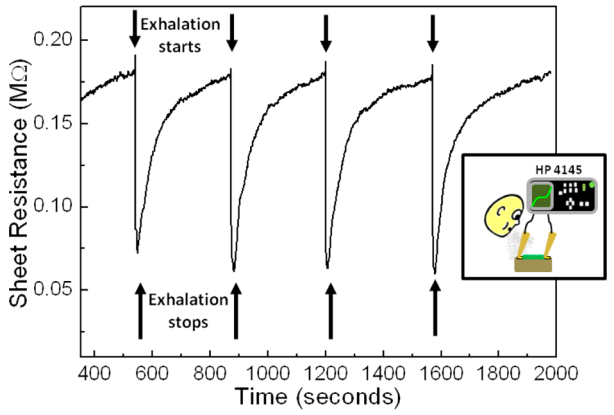

Figure 2. Several cycles of the electrical response of an InGaAs SQD sample to human breath (10 s exhalation). Sheet resistance significantly decreases when exhalation starts. The inset shows schematically the setup used for the measurements.

chemical reactions in similar systems take place due to the interaction of the surface with moisture.[22,23] This result makes evident the high sensitivity of the InGaAs SQDs to the environmental conditions and especially to the humidity.

To quantify the effect of the moisture on the electrical properties of the surface, we conducted an extensive analysis of the impact of the relative humidity (RH) on the sheet resistance of InGaAs SQW and SQDs. To control the RH we used a mixture of dry N_2 and N_2 saturated with water vapor. This mixture is controlled by two needle valves which allow the accurate setting of the relative humidity of the final gas. This resulting mixture is driven to a box where the sample is placed. This box is hermetically closed and a hygrometer is installed inside to monitor the relative humidity within the cavity. To facilitate the measurement, we encapsulated samples in a TO-8, which is connected to the semiconductor parameter analyzer. A sketch of the setup is shown in Figure 3.

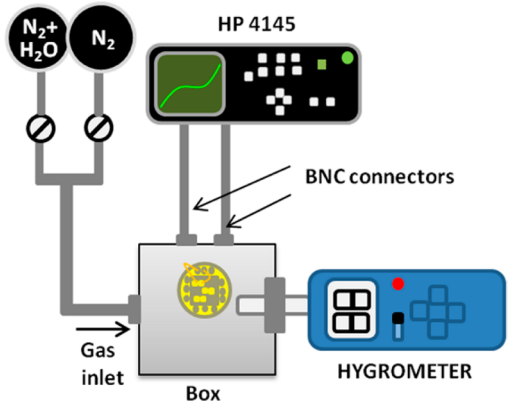

Figure 3. Designed set-up to change and control relative humidity in the surrounding air. A mixture of dry N_2 and H_2O saturated N_2 is used. By means of varying the flux of water vapor and dry N_2, different relative humidity is yield.

The electrical response of the SQDs as a function of the relative humidity is plotted in Figure 4a. Environmental RH varies from 0% to 70% in steps of 10%. It can be recognized a severe dependence of the sheet resistance on the relative humidity yielding to a characteristic value change of more than one order of magnitude from 0 to 70% of RH. When the RH increases, the SR decreases leading to a higher surface conductivity. For a fixed voltage value above 1 V (in both forward and reverse bias) the sheet resistance variation with RH follows an exponential decay law. The behavior is barely dependent on the working voltage (see Figure 4b). The resistance rapidly drops for small changes in the humidity from a dry environment and then tends to saturate. Despite that, it is still possible to monitor differences in the electrical response up to 70% of RH. To conclusively attribute these results to the 3D nanostructures, the experiment of the impact of the RH on the sheet resistance was performed in sample 2. Figure 4c shows the response of SQW sample to different external conditions. It can be observed that the resistance is not affected by the changes in the relative humidity in the atmosphere. A comparison of the electrical response of samples 2 and 3 at −2 V is shown in Figure 4d. The sheet resistance of SQW does not exhibit any correlation with the change of the external conditions. On the contrary, the sheet resistance of the SQDs decreases by more than one order of magnitude when the RH increases from 0 to 50%. The system shows a high sensitivity in this range of humidity. Above 50%, the dependence of the sheet resistance on the RH becomes weaker and the system becomes less sensitive.

The coverage of the surface with adsorbed water molecules can alter the physical properties of the surface. It has been previously reported the effect of such adsorption on the optical properties, attributing the enhancement of the optical emission to the reduction of the density of active surface states after the physisorption process. Surface states are proposed to act as nonradiative recombination centers and thus, their passivation promotes radiative recombination resulting in an improvement of the photoluminescence.[11,16,24] Regarding the electrical characteristics, the decrease in the sheet resistance could also likely be linked to the reduction of the surface states by means of water molecule adsorption, a process that would be enhanced by the high polarity of the molecule.[24] When the state is empty, a carrier can be trapped, lowering the density of carriers on the surface and thus decreasing the surface conductivity. Conversely, when these surface states are linked to water molecules, they turn into nonactive centers, making consequently carrier trapping less probable and leading to an increment in the conductivity. Moreover, Han et al. addressed that on negatively charged oxygen ion surfaces, which is typical in air conditions, the adsorbed water molecules act as electron donors.[19] Thus, water physisorption could not only passivate the surface but also release electrons, which could lower the band bending and promote the carrier's motion. Because the increment of the relative humidity is directly related to the number of water molecules in the surrounding air, the probability of molecule adsorption increases with the RH, giving rise to a less resistive system and therefore, promoting the surface conductivity. Despite of the fact that the number of water molecules can be continuously increased in the atmosphere, the SR reaches a saturation value because the number of available surface states is reduced and new incoming molecules cannot be physisorbed. Thus, understanding surface states as responsible for surface sensitivity, it is plausible to associate the surface passiveness of 2D nanostructures with the lower density of surface states compared to 3D nanostructures, which benefit from the high surface to volume ratio.

In conclusion, a comparison of the electrical properties of InGaAs SQW and InGaAs SQDs referred to a GaAs surface was carried out under different environmental conditions. A

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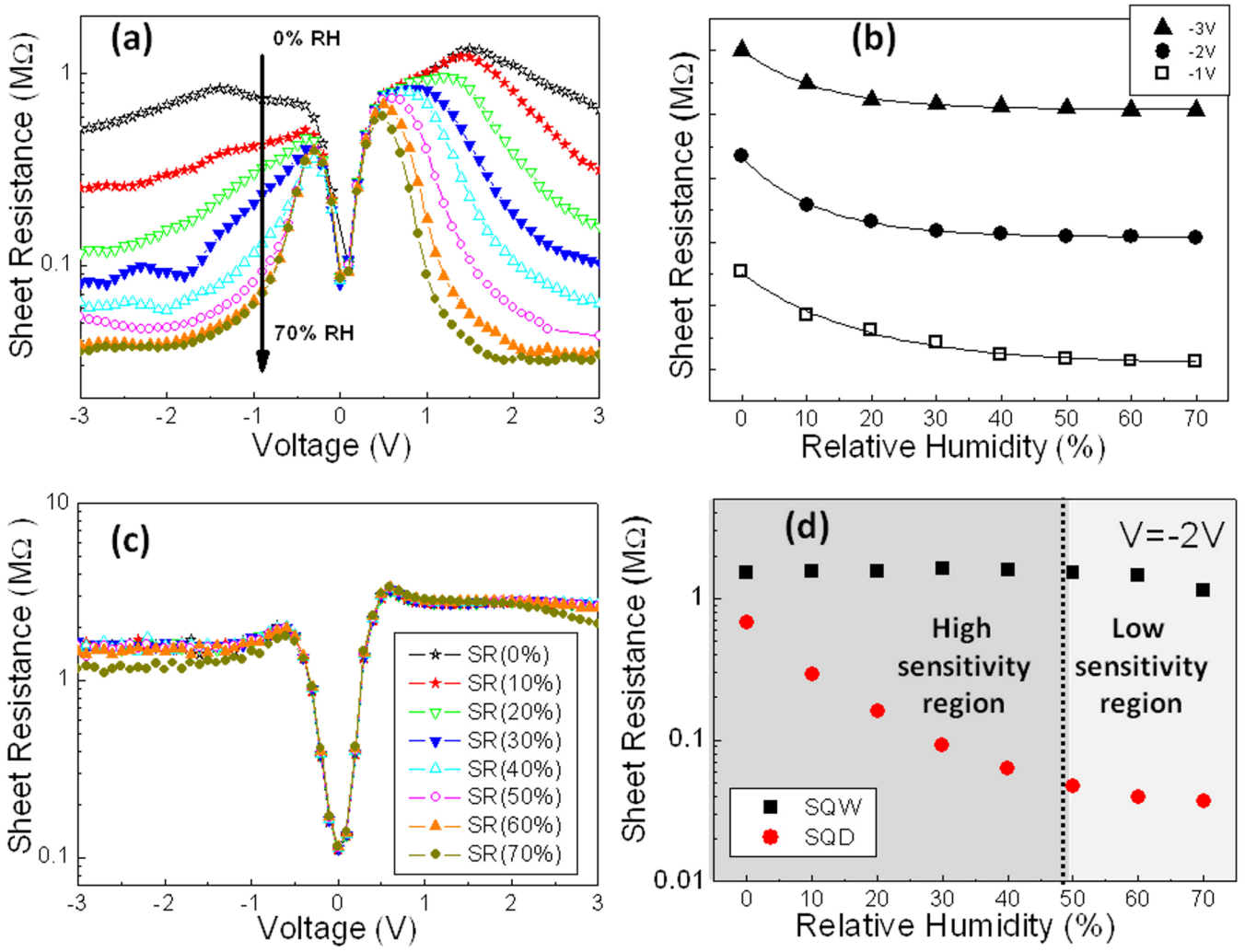

Figure 4. (a) Sheet resistance variation of SQD sample as a function of voltage and relative humidity in the surrounding air. (b) For a set of reverse bias, SR closely follows an exponential decay indicating saturation effects. The curves are vertically shifted for clarity. Continuous lines are exponential fits to the data. (c) SR variation of SQW sample as a function of voltage and relative humidity in the atmosphere. (d) Comparison of the response of SQD and SQW samples to the relative humidity.

detailed analysis of the electrical response as a function of the relative humidity was performed. The results show the high importance not only of the surface composition (InGaAs) but also of having 3D nanostructures for improving the sensitivity of the surface. It was found that the SR of $In_{0.5}Ga_{0.5}As$ SQDs experiments a higher reduction from vacuum to air than that of $In_{0.5}Ga_{0.5}As$ SQW sample, 99% compared to 20%, respectively. Moreover, this sheet resistance decreases more than one order of magnitude when the relative humidity in the surrounding atmosphere increases from 0 to 70%. As a conclusion, we suggest that the adsorption of the incoming water molecules onto the surface reduces the density of active surface states and releases electrons, promoting the electron transport and increasing the surface conductivity. The results reported in this letter demonstrate the great suitability of the InGaAs SQD for sensing applications and make this nanostructure very promising for the development of humidity sensor devices.

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Notes

The authors declare no competing financial interest.

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