The physical reason of intense electroluminescence in ITO–Si heterostructures

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Abstract

Intense electroluminescence from a spray deposited heavily tin-doped indium oxide (ITO)–n type silicon (Si) heterojunctions, presenting the properties of an induced p–n junction, has been observed. The role of the degenerated n-type ITO film as a good supplier of holes to maintain an inversion layer formed at the silicon interface is discussed. However, the physical mechanism responsible for a significantly higher quantum efficiency of the radiation emission from such structures is not clear. The explanation of this phenomenon, based on the confinement of carriers at the interface due to multi-point contacts between the ITO film and the silicon, is discussed.

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1. Introduction

One of the most important fields of current interest in material science is the fundamental aspects and applications of semiconducting transparent thin films such as indium oxide, tin oxide, zinc oxide, and cadmium stannate. The properties of these films, namely a low electrical resistivity and a high transparency, are important for different optoelectronic applications [1]. Due to its transparency and high electrical conductivity, indium-tin-oxide (ITO) films have been widely used as hole injectors in organic light emitting diodes (OLEDs) [2]. These films can be prepared by several processes: sputtering from oxide targets, reactive sputtering using metallic targets, chemical vapor deposition, pulsed laser deposition, and by spray pyrolysis technique. A review of these experimental methods can be found in [1]. The most inexpensive technique, the spray pyrolysis technique, is based on a solution containing salts of indium; the tin is sprayed on a preheated substrate. The formation of the film is achieved due to the chemical pyrolysis of small drops of the solution on the surface of a heated substrate.

Recently, intense electroluminescence was obtained from heterojunctions (ITO–Si) fabricated by spray deposition of the ITO films on the surface of an n-type silicon substrate [3,4]. The ITO films with an optimal content of tin as dopant are degenerated n-type semiconductors, and show a metallic type of conductivity. The Fermi level lies deeply in the conduction band. From this point of view, one can consider the ITO–Si structure as a Schottky metal-semiconductor contact. However, in such contacts a sufficient injection of minority carriers necessary for a radiative electron-hole recombination is not possible. Usually the injection ratio for minority carriers does not exceed $10^{-4}$, even for a high potential barrier [5]. Nevertheless, an injection ratio of about 0.4 has been found in ITO–Si–ITO transistor structures [3]. Detailed studies of the current–voltage and capacitance–voltage characteristics of ITO–Si contacts allowed for the estimation of the energy band diagram of these contacts [6]. As a result, an inversion layer was found at the silicon interface of such structures. This layer is formed due to the high work function of the spray deposited ITO film as well as the special chemical treatment performed on the silicon surface. Thus, the electrophysical properties of the ITO–Si heterojunctions are similar to those of p–n junctions formed using well-known high-temperature methods [5]. In this work we address two important issues: (a) the reason of why a degenerated n-type semiconductor (the ITO film) can provide the holes necessary to support the inversion p-layer at the silicon...
interface; and (b) the high efficiency of radiative electron-hole recombination experimentally observed earlier for the spray deposited ITO–Si contacts. This second issue is important in view of the classical representation concerning the small radiative efficiency of the indirect band gap present in monocrystalline silicon. Hence, new physical processes, such as the quantum confinement of carriers inside the silicon [7], need to be considered as the reason for a high emission from silicon.

2. Experimental details

The spray pyrolysis technique was employed for the deposition of the thin ITO films on sapphire, glass, and silicon substrates. The precursor alcoholic solution was prepared from metallic salts of indium and tin in the form of InCl₃ and SnCl₄, respectively. In order to find the optimal doping, various solutions with different tin concentrations were used. It was found experimentally that the ITO films fabricated at 480 °C and 9% Sn/In ratio in the solution present the highest conductivity and transparency. Further details for the deposition of the films can be found in [8]. The thickness of the films was determined using an Alpha Step. The electric resistivity, Hall mobility, and carrier concentration were measured at room temperature using the standard van der Pauw method. The structural properties were studied using a scanning electron microscope (SEM), and an X-ray diffractometer operating in the Bragg–Brentano Θ–Θ geometry with copper radiation. The transmission spectra of the ITO films deposited on a sapphire substrate were recorded using a double beam spectrophotometer. The ITO–silicon structures with 100 nm thick film were fabricated on an n-type silicon wafer with a resistivity of 10 Ω cm. Further details of the preparation of the silicon substrates as well as the methods used for the characterization of the ITO–Si structures, were reported earlier [4].

3. Results

3.1. Properties of the spray deposited ITO films

The ITO films prepared under optimal conditions present an electrical resistivity of about 2×10⁻⁴ Ω cm and optical transmittances of 76–85% in the visible range; these values are comparable to those reported in [9]. The structural properties of the ITO film fabricated at 480 °C, obtained with the X-ray diffraction and SEM techniques (left inset), are shown in Fig. 1. A comparison with tabulated In₂O₃ powder data [10] clearly shows the cubic structure of these ITO films, and a preferred <400> orientation of grains perpendicular to the substrate plane was observed. Diffraction patterns show only In₂O₃ peaks. The inset on the right of Fig. 1 shows the face plane of the cleaved Si-substrate with the ITO film deposited on the surface. One can see that the preferred (400) orientation of the grains determines a columnar structure of the ITO film. The inset on the right of Fig. 1 also shows an enlarged image of the boundary between the silicon substrate and the film. One can see that the non-uniform ITO–Si boundary presents the characteristics of multi-point contacts. We will discuss below the possible influence of this contact topology on the radiative properties of the ITO–Si structures.

3.2. Radiative properties of the spray deposited ITO–Si structures

Fig. 2 shows the electroluminescence (EL) spectra obtained experimentally for the ITO–Si structure when a positive voltage is applied to the ITO-electrode. For the sake of comparison, the radiative emission from silicon p–n diodes [11] and Al–SiO₂–pSi surface–barrier structures [12] is shown in the same figure. The emission efficiency from texture-oriented p–n diodes reported in [11] is about 10⁻², whereas the one obtained from the surface–barrier structures [12] is very low, about 10⁻⁶. In our structures, the estimated efficiency reaches values of 10⁻⁴–10⁻³. Further details of the electro-physical properties of these
ITO–Si structures have been reported earlier [3,4,6,8], and we invite the interested readers to consult our previous work.

4. Discussion

As was noted in the introduction, a sufficient radiative emission from metal–silicon Schottky diodes is impossible to obtain because of the very low value of the minority carrier injection ratio. Because of the high barrier height (0.8–0.9 eV), our structures show the properties of a p–n junction, in which the surface inversion p-layer is formed by a large band bending at the silicon surface (Fig. 3).

Thus, holes injected from the inversion p-layer can recombine radiatively with electrons in the silicon substrate. How the degenerated n-type ITO film serves as supplier of the holes necessary to form such inversion layer? We considered this question in details recently [13], and such possibility really exists for a heavy-degenerated ITO films with a $10^{21}$ cm$^{-3}$ electron concentration, when the shift of the Fermi level into the conduction band is nearly 0.6 eV. Under such circumstances, the difference between the Fermi level and the bottom of the silicon valence band (Fig. 3) is about 0.3 eV at the ITO–silicon interface. The tail of the Fermi distribution at room temperature gives a sufficient probability for the transition of electrons from the silicon valence band to non-occupied energetic states inside the ITO conduction band. The number of such states is essentially high enough to support the holes concentration in the inversion layer at the silicon interface [13]. Experimental results reported earlier [3] show a high value (~0.4) of the minority (holes) injection ratio in the ITO–nSi contacts fabricated using spray pyrolysis.

Fig. 4 shows one-dimensional simulations of the distribution of injected carriers (holes for the inversion layer and electrons from the n$^+$-contact fabricated on the back side of the silicon substrate), obtained for a barrier height of $\phi_B=0.89$ V; the carrier concentration in the silicon substrate, holes at the silicon surface, and electrons in the n$^+$-contact, were $3 \times 10^{15}$ cm$^{-3}$, $5 \times 10^{18}$ cm$^{-3}$, and $10^{19}$ cm$^{-3}$, respectively.

The calculated injection ratio for the minority carriers in the case of a barrier height from 0.8 to 0.9 eV, and a peak pulse current density of $6 \times 10^4$ A/cm$^2$, was 0.6–0.8. From Fig. 4 one can see that the maximum concentration of injected electrons and holes is located at a distance of about 0.1 \( \mu \)m from the silicon surface. Accordingly, the estimated injection is enough for a high radiative emission from the silicon. However, the quantum efficiency experimentally obtained from standard (not specially designed as in [11]) p–n silicon structures is of the order of $10^{-6}$ [14] due to the emission of phonons that must take place to satisfy the momentum conservation in indirect band gap semiconductors. Moreover, a low efficiency occurs due to the
diffusion of injected carriers to non-radiative recombination centers and defects.

A higher efficiency can be obtained through the spatial confinement of the injected carriers in the potential wells specially created near the $p-n$ junction, as it was demonstrated in [7] using $p-n$ structures and engineering of defects that originated these potential wells. For the ITO–nSi surface–barrier structures the reason of improved quantum efficiency can be explained by considering the morphology of the contact between the ITO film and the silicon (Fig. 1). Every grain of the ITO column leads to quasi-spherical point contact with the silicon surface (see the inset on the right of Fig. 1). In this case, the ITO film serves as perfect supplier of holes to form the inversion $p$-layer. However, these point ITO–Si contacts are separated by small-size hollows, which are due to the columnar structure of the ITO film. Taking into account that above these hollows the indium oxide columns present an electrical contact, this representation of the ITO–nSi structure can be represented as a parallel connection of point $p-n$ diodes with surrounding ITO–air–Si capacitors as shown in Fig. 5. This parallel structure is connected in series with the resistance of the silicon substrate.

When a positive voltage is applied to the ITO electrode, the capacitors surrounding the forward-biased point $p-n$ diodes operate in the accumulation mode, and electrons are stored in the potential well at the silicon interface. At the same time, a high hole concentration in the inversion layer at the silicon surface also takes place below the point ITO contact. Thus, a spatial confinement of electrons and holes at the silicon surface is obvious. This carrier confinement in the potential wells allows for the partial removing of the requirement of momentum conservation because it facilitates the formation of excitons (in this case the interaction of only two particles, namely exciton and phonon), takes place instead of the interaction between three particles: electron, hole, and phonon); and as a result, the radiative recombination of carriers increases. The results reported by Lin et al. [15] can serve as the evidence of the legitimacy of our model. In that work metal–oxide–silicon (MOS) structures with a radiative efficiency above $10^{-4}$ were fabricated by depositing aluminium on the silicon surface covered by $\text{SiO}_2$ nanospheres ($\sim 12 \text{ nm in diameter}$). The layer of Al penetrates in the several hollow spaces between these particles forming multiple Al-Si point contacts surrounded by MOS structures (Fig. 6).

Thus, the design of the device reported in [15] is quite similar to the structure reported here. Authors of [15] also explain an improved efficiency using spatial confinement of electrons and holes near the Si–$\text{SiO}_2$ interface. Such confinement of carriers allowed them for observing near-lasing actions such as threshold behavior and resonance modes corresponding to the silicon band gap energy.

5. Conclusions

The improved quantum radiative efficiency from these structures, that possess the properties of an inversion $p-n$ junction with the ITO film operating as the holes supplier, is explained by the topology of the ITO–Si contact. It was found that this contact has a multi-point nature due to the columnar structure of the ITO film. Using this experimental fact, the model of spatial confinement for carriers at the silicon surface is proposed. This confinement of carriers allowed for explaining satisfactorily the improved efficiency for the radiative emission as a result of a partial removing of the requirement for momentum conservation that limits the radiative efficiency in indirect band gap semiconductors.

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