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CURRENT STIMULATED ELECTRON AND PHOTON EMISSION FROM ADLAYER-COVERED NANOMATERIALS

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Abstract

We review experimental investigations of the effect of electropositive and organic overlayers on electron and light emission from nanodispersed (metal and semiconductor) thin films excited by the conduction current. Possible mechanisms of the emission are discussed.

1. Introduction

Nanomaterials science in all its branches and nanoelectronics are exploiting various kinds of size effects which set in as the reducing dimension of an object becomes equal to some characteristic length. In this work we will consider electron and light emission phenomena which occur when electric current is passed through a system of nanoparticles. The nanoparticles are located at small (also nanometer) distances from each other which makes the potential barriers between them sufficiently transparent for electrons. Thus the nanoparticles are integrated by electron tunneling into a unified system. At the same time the coupling between the particles is not so strong as to deprive them of their nanospecifics. Dispersed thin films consisting of metal islands on dielectric substrates are an example of such systems.
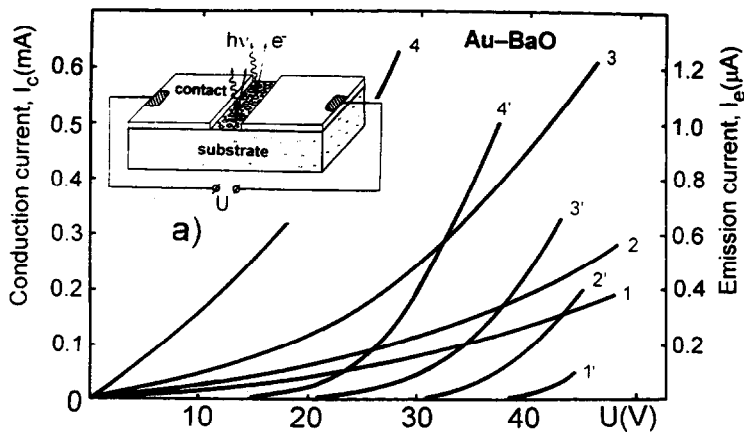
The island films (IF's) were shown to emit electrons and light when excited by the conduction current or electromagnetic irradiation (see the original work [1] and later reviews [2-5]). It has been found that experimental data on these phenomena can be interpreted most satisfactorily in terms of the nonequilibrium heating of electrons in nanoparticles. The possibility of such heating is primarily a consequence of the strong size effect in the electron-phonon interaction: when the particle size is

smaller than the electron mean free path in the volume, the transfer of energy from the fast electrons to the crystal lattice is dramatically suppressed. This idea was presented in detail in [4, 6, 7]. Additional factors which enhance the deviation from equilibrium between electrons and phonons in small particles will be listed in Sec. 3 A.

Here we report on further investigations of the emission phenomena in island thin films.

2. Experimental

The IF's under study were prepared by vacuum evaporation of Au, Ag and C on glass, quartz glass, mica, SiOx and other similar substrates provided with previously deposited electrical contacts (Fig. 1). The current-voltage characteristics of the conduction current and emission current as well as the light emission intensity were recorded in both the DC and AC voltage regime.
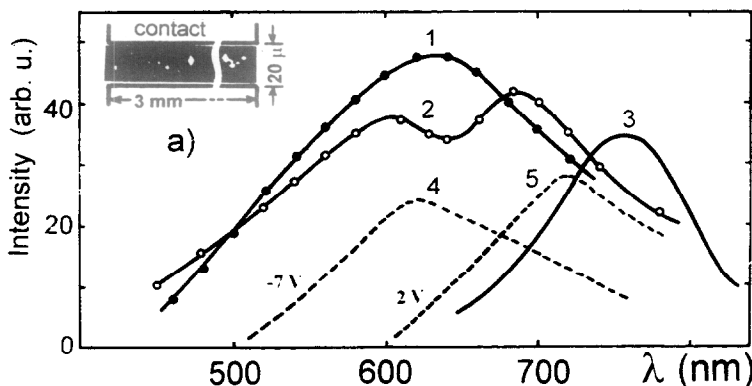

Fig. 1. Schematic of the island film (a); I-V curves for conduction current (1-4) and emission current (1'-4'). Curves 1 and 1': clean Au film; curves 2-4 and 2'-4': Au film with various BaO overlayers.

The film structure was examined by scanning and transmission electron microscopy. Some emission experiments were made immediately in the column of the transmission electron microscope. In this case the films were prepared on SiOx substrates ($\approx$50 nm thick) transparent for the electron beam. The measurements of the electron and light emission were made both for the entire film (integrally) and for separate emission sites.

It will be recalled that the electron and light emission from IF's excited by the conduction current is observable after the creation of "current channels" in the films. The channels are formed by electromigration and represent percolation paths [8]. For the film geometry depicted in Fig. 2 (inset), typically a few tens of the current channels are formed. No more than one emitting site can appear in each channel. The sites emit simultaneously electrons and photons and have a size of $\leq$0.5 μm. They

were shown to arise in the areas with a favorable mutual arrangement of adjacent islands where a larger ($\sim 10^2$ nm) island is surrounded by nanoislands [2, 9]. The formation of the current channels is facilitated when the film is deposited on a grooved substrate and due to this consists of the chains of islands stretched between the contacts [4, 10].

Fig. 2. (a) Light emission sites in an **Au** film. Light emission spectra: (1), (2) for two sites in the same **Au** film; (3) for a chain **Au** island film ; (4), (5) for an **Au/W** tunnel gap in STM [11, 12].

The electron and light emission arises in the non-Ohmic region of the conduction current-voltage curve at average field strengths of $\geq 10^4$ V/cm (Fig. 1, curves 1 and 1'). All the measurements were made under vacuum of $\sim 10^{-8}$ Torr.

To obtain a **Si** island film, we first deposited epitaxially a continuous single-crystal n-**Si** film (100 nm thick, 10 Ohm·cm) on a sapphire substrate. The continuous film had in the middle a section 50 μm wide where its thickness was 50 nm. The contacts were evaporated on the thicker parts of the film. The film was first outgassed at $\sim 10^{-8}$ Torr and then a sufficiently strong current was passed through it which led to the formation of a **Si** island film in the thinner part of the sample. For comparison, some experiments were made with a porous **Si** sample prepared by electrochemical etching.

3. Effect of Overlayers on Electron and Light Emission from Island Metal Films

A. Electropositive overlayers

The evaporation of **BaO** on IF's leads to a significant increase of the conduction current (Fig. 1, curves 2-4) and to a drastic, by several orders of magnitude, growth of the emission current (Fig. 1, curves 2'-4'). Both the effects can be ascribed to the reduction of the work function. The variation of the work function was monitored by recording the shift of the red boundary of photoemission from a *continuous* **Au** film deposited adjacent to the island film and exposed to the same **BaO** molecular beam.

The model of nonequilibrium heating of electrons in small particles [4, 6, 7] interprets the observed electron emission from IF's as the Richardson emission of the hot electrons. With this assumption we used the work function dependence of the emission current to estimate the electron temperature T_e and obtained its value at ~2000 K. Contrary to this, the lattice temperature of the islands remains much lower which ensures the long-term operation of such IF cathodes [4]. Along with the weak electron-phonon coupling mentioned in Sec. 1, there are additional factors which are favorable for the strong difference between the electron and lattice temperature of small particles: (1) the possibility of pumping high power densities into their electron gas (via the high-density conduction current or intense and strongly absorbed electromagnetic irradiation); (2) the strong cooling of the lattice of islands due to fast heat dissipation in the substrate [4-6].

As seen from Fig. 2 (curves 1, 2), the spectra of the light emitted from different sites of the same IF can be rather different. The spectra of the emitting sites in the chain island films appear much more uniform (Fig. 2, curve 3). The **BaO** deposition within the limits of a monolayer affects mainly the intensity of the emitted light while its spectrum remains almost unchanged. It is interesting to note that the spectral composition of the light radiated from IF's bears similarities to that of the light emitted from the tunnel gap (tip/surface) in STM (Fig. 2, curves 4 and 5). In the latter case the light was shown to have a significant contribution from radiative relaxation of local surface plasmons generated in the course of inelastic tunneling of electrons [11, 12]. This point was discussed in more detail in Ref. 5.
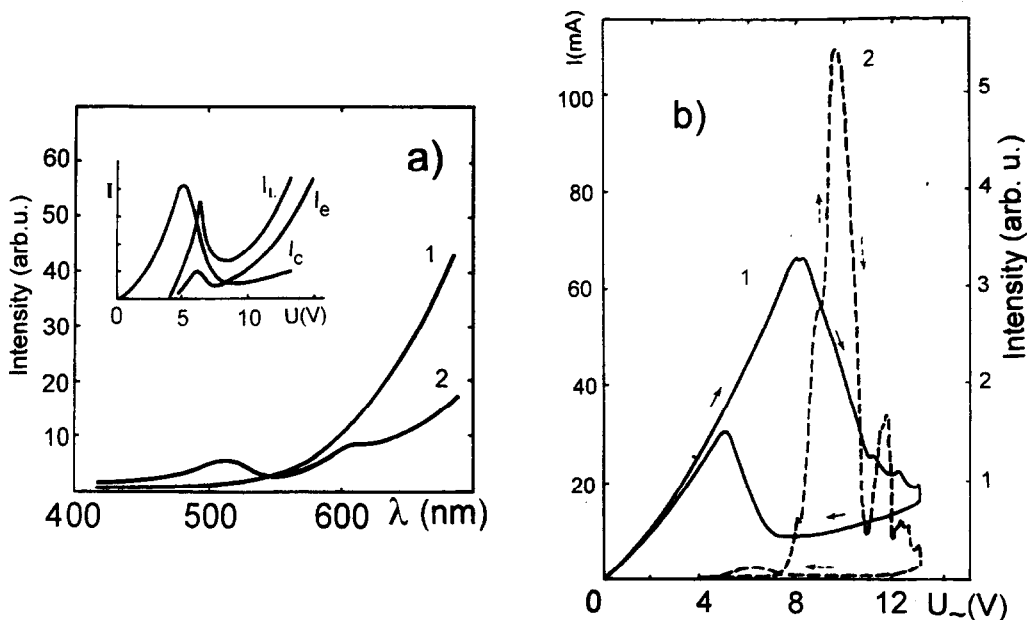
If the **BaO** coating over an IF is only about 1 monolayer thick, the emission current, which is initially very strongly enhanced, decreases with time to a new steady-state level which still remains much higher than in the absence of the **BaO** layer. The measurements of the emission current-voltage curves for individual emission sites performed in a quasi-spherical retarding field have shown that the decay of the emission current is caused by some work function increase. Probably this can be associated with the drift of **BaO** molecules out of the emitting sites [13, 14]. To ensure a long-term effective electron emission, with an emission to conduction current ratio of $\approx$10-15 %, it is necessary to provide a continuous supply of **BaO** to the emitting sites. This effect is achieved by deposition of IF's onto a substrate previously coated by a thick **BaO** layer. In such a case, especially when large emission currents were extracted, we observed significant changes in the spectrum of the emitted light due to electroluminescence of **BaO** itself.

A similar effect of **BaO** as well as **Ba** overlayers on the electron and light emission was also found for graphite IF's. These films were excited both by the conduction current and by pulsed CO_2 laser irradiation (λ=10.6 μm, τ=200 ns).

B. Organic overlayers

In these experiments, an overlayer of stearone [$(C_{17}H_{35})_2CO$] was evaporated on IF's with previously formed current channels and emission sites. The evaporation was performed while a voltage of $\approx$10-15 Volts was applied to the film. Stearone molecules adsorbed under such conditions also induce an enhancement of the conduction current. What is more important, the conduction

current-voltage curve acquires a nonmonotonic (N-shaped) character: there appears a section of the voltage controlled negative resistance (VCNR) at voltages ≈4-6 V (Fig. 3 a, curve I_C in the inset). Simultaneously the characteristics of electron and light emission are also changed (Fig. 3, curves I_e and I_L in the inset).

Fig. 3. (a) Inset: conduction current I_C, emission current I_e and light intensity I_L versus AC voltage applied to an **Au** island film covered with stearone. Scales for I_C, I_e and I_L are different. (1) and (2) are light emission spectra in rising and falling section of the I_C-V curve. (b) Hysteresis loops for the conduction current (1) and light intensity at λ=615 nm (2) measured for an **Au** film covered with stearone. Voltage frequency: 500 Hz. Sweep time: ≈2 min.

It should be stressed that, contrary to the case of **BaO**, organic admolecules increase the conduction current only upon holding the film under a voltage of 10-15 V either in the course of evaporation of the organics or after it. It has been suggested that the admolecules are polarized in the high electric field and pulled into the emission sites where they self-assemble into thin quasi-polymeric filaments spanning the gaps between the islands. It should be recalled that the formation of molecular wave guides for electrons was observed a few decades ago in experiments with organic molecules adsorbed on metal tips in the field emission microscope [15, 16]. The average diameter of the polymeric filaments, oriented along the field lines, was estimated at several nm [17], i.e. the same as the size of nanoislands. If similar organic bridges are formed in IF's, the current density in them should be at least ~10^5 A/cm^2 at the emission current of ~10^{-8} A. Probably, such a high current density could be passed without destructing the filaments because of the very efficient withdrawal of the Joule heat to the substrate. However, at higher current densities the conducting filaments can be disoriented or even evaporated which may cause a decrease in the conduction with increasing

voltage. When the voltage is reduced, the organic conducting bridges can be restored (replenished) by migration of the adsorbate from adjacent areas to the emission sites. This "thermal" model might, in principle, explain qualitatively both the occurrence of the N-shaped I_C-V curve and its repeated reproduction while increasing and decreasing the voltage.

However, the data on the light emission from IF's covered with organics impel to consider an alternative model. Fig. 3 b displays a close correlation between the changes of the conduction current and light intensity (λ=615 nm). These results recorded in the alternating voltage regime show that the hysteresis loop for the light intensity represents rather closely the modulus of the derivative of the loop for the conduction current. Such a behavior is quite typical for electroluminescence of semiconductors (see e. g. Ref. 18,19).

Thus we suppose that what is observed in our case may be the electroluminescence of organic bridges which are excited by hot electrons injected into them from adjacent metal islands. In this approach, the VCNR region in the conduction current-voltage curve can arise due to one of the mechanisms known for semiconductors. It would now be premature to suggest a more exact model for this process.

There is a considerable difference between the light spectra corresponding to the rising and falling (VCNR) sections (Fig. 3 a). In the former case the spectrum is nearly structureless, but shows a steep intensity growth in the red and infrared region (λ>600 nm). In the latter case there are two broad maxima at $\lambda \approx$510 and 610 nm, and the intensity strongly increases at λ>700 nm. Both the spectra are distinct from the spectrum for clean gold IF's (Fig. 2) which shows a number of pronounced maxima in the visible region. Possible light emission mechanisms for this case (*bremsstrahlung*, inverse surface photoeffect, surface plasmon radiation etc.) were discussed elsewhere [4-7].
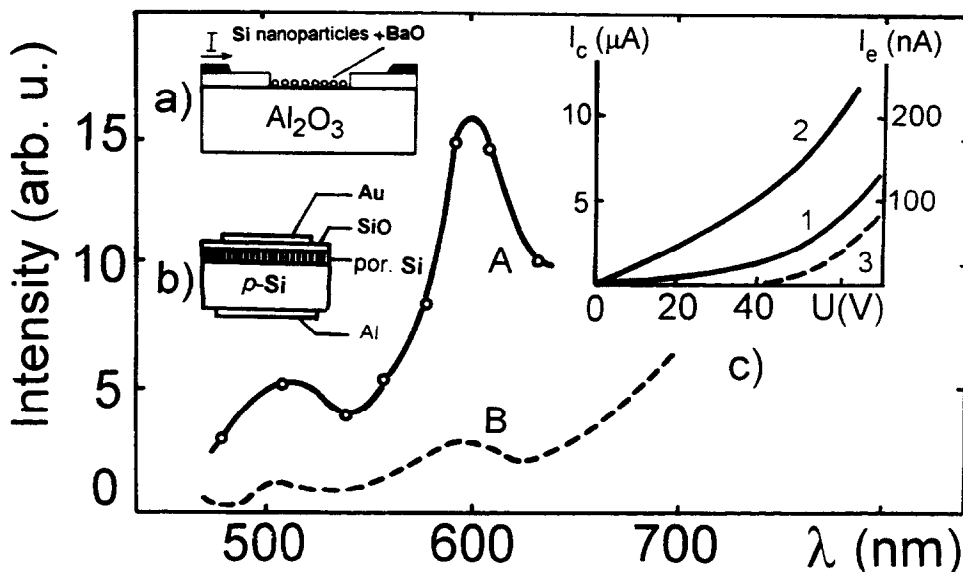
It should be noted that the slope of the VCNR section is an integral characteristic of the entire film which contains many current channels with somewhat different properties. Therefore the peculiarities seen in the VCNR in Fig. 3 b may stem from contributions of different channels. For the chain island films, where the current channels seem to have rather close parameters, the VCNR section appears very steep so that one observes actually a switching regime.

Quite analogous effects were observed with naphthalene ($C_{10}H_8$) overlayers evaporated on the island films.

4. Electron and Light Emission from Silicon Island Films

The conduction current I-V curves for clean silicon IF's are quite similar to those for metal IF's (Fig. 4), but neither electron nor light emission is observed until the work function of Si islands is reduced by some suitable overlayer (e. g. **BaO**). Thus, the hot electrons which can be generated in Si islands cannot pass into vacuum if the Si surface is clean. This result is reminiscent of the experiments carried out in an attempt to obtain electron emission from Si p-n-junctions cleaved in high vacuum [20]. Again, no emission was observed in that case, which was attributed to the unfavorable

relationship between the impact ionization energy (2.25 eV) and the electron affinity (3.6 eV) in Si. Due to this, the electrons cannot be heated enough to overcome the surface barrier. The emission emerged upon reducing the Si work function by a few eV's.

Fig. 4. (a) Structure with the island Si film; (b) structure for observation of electroluminescence of porous silicon; (c) I-V curves for conduction current of clean silicon IF (1), **BaO/Si** IF (2) and for emission current from **BaO/Si** IF (3). (A) and (B) are light emission spectra for structures a and b.

In the case of Si island films, the evaporation of a **BaO** overlayer lowering the work function by 2.2-2.5 eV resulted in a substantial enhancement of the conduction current and in the appearance of the electron and light emission (Fig. 4).

We have compared these results with data on electroluminescence and electron emission from a porous Si sample prepared by electrochemical etching of p-Si (0.01 Ohm·cm) plates. The size of the pores and the thickness of the walls between them was ~5-10 nm. A sandwiched test structure was used (Fig. 4). The electroluminescence and electron emission were observed for as-prepared samples (no activating coating was needed). The spectrum of the electroluminescence of the porous Si is rather similar to that recorded for the Si island film covered with **BaO** (Fig. 4). It was found, however, that both the electroluminescence and the electron emission disappear after outgassing the porous Si sample. They could be restored after H_2O adsorption [21], which demonstrates that surface conditions strongly affect the behavior of porous Si. These data will be published in more detail in Ref. 22.

5. Conclusion

The deposition of various overlayers on nanodispersed thin films, both metal and semiconductor, allows a wide range modification of their electron and light emission properties. In particular, using this approach one can obtain planar composite structures whose characteristics combine the peculiar properties of nanoparticles and of the substance filling the gaps between them.

Acknowledgements

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