PHOTOEMISSION INVESTIGATIONS OF NON-METAL/METAL TRANSITION IN THIN DISCONTINUOUS ANTIMONY FILMS

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The electric and photoelectric properties of very thin discontinuous antimony films deposited on an insulating (sapphire) substrate were investigated in order to explain the "surfactant" role of Sb atoms in the growth of other metal films on this substrate. The results show that the properties of pure Sb films on a sapphire are similar to those observed for other metals and cannot explain an essential change in the growth of Ag, Au, Ga and other metals when the substrate is pre-germinated with antimony.

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1. Introduction

One of the most important problems of the modern microelectronic technology is the production of semiconductor heterojunctions without defects and strains at the interface of two different solids. Even in the conditions indispensable for an epitaxy, the growth of one material on another can lead to islanding due to different values of their free surface energies. For example, Si grows on Ge(001) in the Volmer—Weber mode, whereas Ge grows on Si(001) in the Stranski—Krastanov mode [1, 2]. A new possibility of changing the growth mode of such structures was indicated by Copel and co-workers in 1989. By vacuum evaporation at the interface of both semiconductors they deposited a very small amount (of about one monolayer) of As [3], or Sb [4]. Atoms of these surface active species (surfactants) change the energy of the substrate—vacuum interface and float at the growth front without being incorporated. The free surface energies of Ge and Si at the interface are much lower with a monolayer of Sb than without it. This enables an island-free growth of Ge on Si and vice versa. In a similar manner, a layer-by-layer growth was also achieved with the use of surfactants during the deposition of Ag on Ag(111) [5] and Co on Cu(111) [6]. The Volmer—Weber growth mechanism (islanding) is dominant for thin metal films on insulating substrates such as glass, quartz, sapphire, rutile, etc. Recently, there was published the first paper showing a surfactant
effect of CO on the growth of Pt on an insulating TiO$_2$(110) crystal [7]. We found out that the presence of Sb atoms on a sapphire substrate can modify the growth of thin Ag films on this substrate [8]. In papers [7] and [8] an important flattening of metal islands was observed, although an ideal layer-by-layer growth was not achieved. This flattening is revealed by the lower value of the Ag-film thickness at which the conduction percolation current appears. In the present work we studied how the electric and photoelectric properties of pure antimony films on a sapphire substrate differ from those of other investigated metals, in order to find a cause of their surfactant behaviour.

2. Experimental

The experimental details were published elsewhere [9]. The experiment was performed in a typical stainless-steel UHV apparatus at a residual gas pressure $p < 10^{-7}$ Pa. Antimony was evaporated from a molybdenum boat with an evaporation rate of 0.02 nm/s, controlled by a quartz resonator and an appropriate electronic set, co-working with a PC computer. A sapphire plate Al$_2$O$_3$(110) was used as a substrate. It was $20 \times 15 \times 2$ mm in size and was maintained at room temperature. Photoemission was excited by 4.8 eV photons dispersed from a mercury UV lamp by using a quartz-prism monochromator. Photoelectron energy spectra were measured with a 127° electron energy analyser of the Hughes-Rojansky type. All procedures were controlled and registered by a PC computer. By integrating the electron energy distribution curves the dependence of the integral photoemission current (PhC) on the antimony film thickness was obtained. The electric conduction current (CC) of the film measured at a constant potential difference of 1 V varied from $10^{-10}$ to $10^{-3}$ A.

3. Results and discussion

Similarly as in the investigations of other metals deposited on an insulating substrate the photoelectron energy spectra for thinner Sb films are broadened and shifted with respect to those characteristic of well conducting thick films [9, 10].

In Fig. 1 a set of such spectra for six different thicknesses of the antimony film is presented. These curves have been selected from among many others to demonstrate the main tendency of changes. As a zero energy, a point was chosen corresponding to the right side cut-off of the spectrum characteristic of a thick continuous film. It corresponds to a Fermi level position in a metal. For the thinnest film (curve 1, $d = 3.2$ nm), a peak of the emission intensity is observed at the energy varying from $-2.5 \text{ to } -3.0$ eV. When the film thickness increases, this peak shifts initially to a lower energy range, between $-3.3 \text{ and } -3.8$ eV for a layer 48.4 nm thick (curve 2). For thicker films the peak shifts to a higher energy (curve 3), similarly as it was reported for Ag, Au, Ga and for the Sb-modified growth of Ag films [10]. Simultaneously the width of the energy spectrum (curves 4, 5, 6) and the photoemission intensity increase. For a film thicker than 80 nm, the position and width of the peak is typical of a thick, freshly evaporated Sb and does not change with the increasing thickness. Figure 2 shows the dependence of the integral photoemission intensity and conduction current on the Sb film thickness. A dramatic growth of the photocurrent intensity is observed when
Comparing the electric and photoelectric properties of antimony (the present paper) and other metal films [9, 10], we can see that:

1. The percolation conduction current appears for Sb and Ag at a relatively high film thickness, of about 40–50 nm. For gold this thickness is lower, as it grows as a more dispersed film, composed of smaller islands. We think that an antimony film, near the percolation threshold is built up from rather big islands. An STM investigation can verify this supposition.

2. The dramatic increase in the conduction and photoemission currents is the film thickness exceeds 52 nm. A similar effect for the conduction current takes place at 55 nm (curve 2).

Fig. 1. Photoelectron energy distribution curves for thin antimony films deposited on a sapphire substrate. The film thicknesses for particular curves are: 1 — 3.2 nm, 2 — 48.4 nm, 3 — 51.6 nm, 4 — 53.2 nm, 5 — 54.8 nm, 6 — 84 nm.

Fig. 2. The dependence of the conduction current and integral photoemission current on the Sb layer thickness.
observed for an Sb film practically at the thicknesses of 52 and 55 nm, respectively (Fig. 2), whereas for silver the difference between the appearance of both currents is significantly greater and corresponds to thicknesses of 25 and 45 nm [9].

3. The current vs. thickness dependence in the percolation range has a greater slope and the percolation range is narrower than that reported for Ag [9]. This may be useful in the construction of very sensitive microsensors.

4. The problem of charging the Sb-islands is more complicated. This is revealed by the shift of a photoelectron energy peak during the growth of antimony films initially to a lower energy, which was not observed in the case of silver [9], gold and gallium [10] films.

4. Conclusions

Although the electric and photoelectric properties of a pure antimony film deposited on a sapphire substrate differ in some details from those of Ag, this cannot explain its role in the growth of thin films of other metals on an insulating substrate. It seems that the "surfactant" activity of Sb atoms is revealed when they are placed in interfacial positions between two solids (Si/Ge, Ag/sapphire, etc.).

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References