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Ellipsometrical studies on the Au/Si(111) system

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Abstract

An experimental arrangement is described which allows the deposition of thin gold films on Si(111) single-crystals and the in situ optical characterization at various temperatures, thicknesses, and angles of incidence of the light. The optical analysis is performed with the help of a highly sensitive spectroscopic ellipsometer operating in the wavelength range 400–900 nm. Additional structure information is obtained from REM, LEED/Auger, X-ray and resistivity measurements. The gold films exhibit a homogeneous single-crystal structure after deposition at room temperature. With increasing annealing temperature the films crack and form an island-shaped eutectic Au/Si melt, cooling leads to a decomposition of the binary mixture and formation of gold islands embedded in the silicon surface. The eutectic temperature is found to be smaller than in bulk samples with a marked hysteresis in the Δ or ψ vs. T curves. The wavelength dependence of ψ shows, in addition to the well-known interband transition of gold, a resonance at about 570 nm. It can be traced back to a Mie plasmon excitation in the solid gold islands which disappears in the liquid state. © 1998 Elsevier Science S.A.

Keywords: Ellipsometrical studies; Au/Si(111) system; Optical properties

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1. Introduction

The Au/Si system is of particular interest with respect to the application (contacts in microelectronic devices) as well as to basic research (very low eutectic temperature). In a previous paper [1] we have produced eutectic melts by depositing thin gold layers on Si(111) single-crystals at room temperature and subsequently annealing at temperatures above 320°C. The solid/liquid transition was studied with the help of X-ray diffraction and resistivity measurements. A lowering of the eutectic temperatures was found as compared to the bulk value. Aim of the present paper is to include optical measurements into discussion. Silicon is more or less transparent in the visible and near IR spectral region. Consequently, the gold film can be detected with high sensitivity even if rather thin layers are deposited. We will concentrate in the present investigation on the phase transition from the solid to the liquid state which should be directly reflected in the ellipsometrical response and its wavelength dependence.

2. Experimental

The cell shown in Fig. 1 is made of stainless steel. The whole vacuum apparatus including pumps and pressure control unit can be moved out of the ellipsometer on precision rolls in order to make possible a heating of the cell without warming up the sensitive optical elements like polarizer/analyzer or compensator. The flexible coupling in the center of the turning axis of the ellipsometer as well as a cardanically mobile support of the cell provide sufficient adjustment facilities to make sure that the fixed light beam impinges on the sample under very defined conditions. The silicon substrate (111-orientation, dimensions $10 \times 5 \times 1$ mm^3, p-doped, $\rho \approx 2\ \Omega$ cm) is mounted in two holder sheets made of tantalum which allow a quick exchange of the samples under investigation, and a direct current heating as well. The temperature is recorded by means of a Ni/CrNi thermocouple fixed on the tantalum sheets. Calibration measurements have shown that the accuracy of the temperature determination is about 5%. The gold is evaporated from a tungsten helix with a molten-on pearl of specpure gold [1]. The evaporation rate can be easily adjusted to 1 nm/min by varying the heating current of the helix and recording the thickness of the film with the help of a vibrating quartz thickness monitor (Kronos FTT 300). The annealing temperature is adjusted

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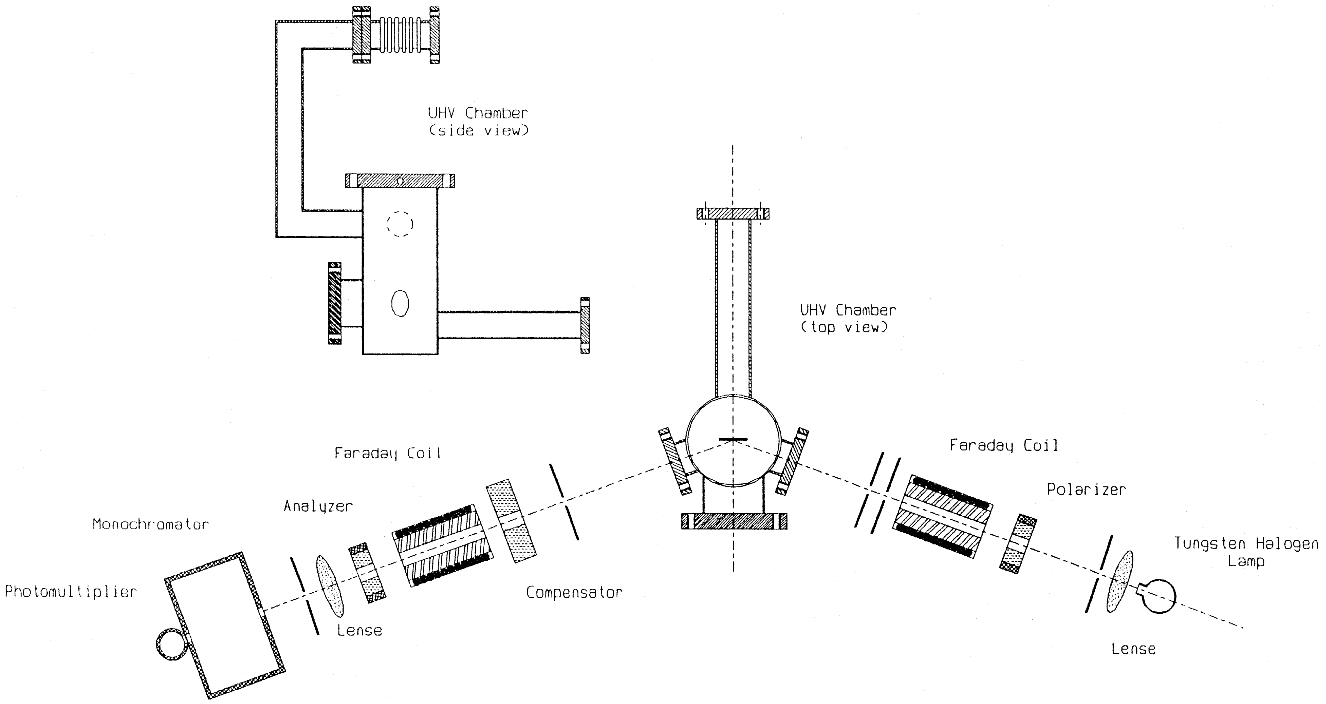

Fig. 1. Schematic representation of the experimental set-up.

to the desired value either by an indirect ($T < 500$°C) or by the direct current heating ($T > 500$°C). The light passes through two glass windows of an area (diameter 40 mm) sufficient to make possible the investigation of the ellipsometric response on a change in the angle of incidence in the range 60°–80° [2].

The ellipsometer used for the present studies has been described in detail elsewhere [3]. A tungsten band lamp serves as the light source in the wavelength range 400–900 nm. The polarizer and analyzer azimuths were modulated periodically by means of magneto–optical rotation of the plane of polarization. The final angular positions of both optical elements were optimized by an on-line computer using a lock-in technique for the detection of the signal. At the same time, the Soleil–Babinet compensator was automatically kept at the quarter-wave position. The computer put out the results in terms of the phase shift Δ and the amplitude ratio ψ [4].

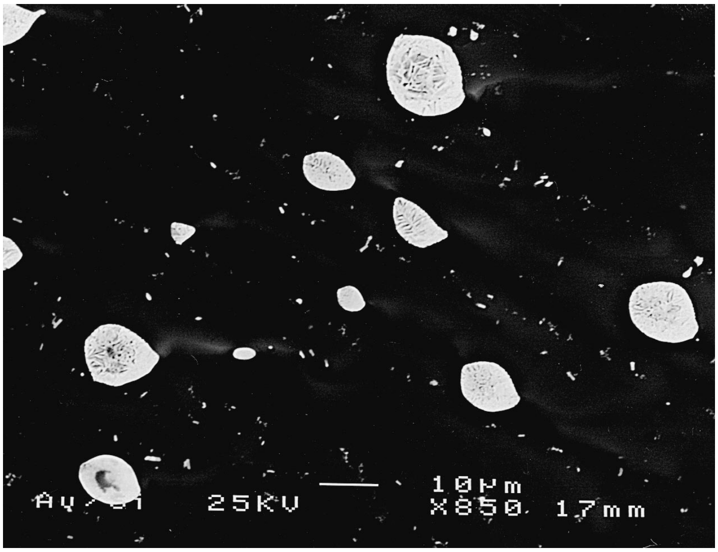

Fig. 2. REM micrograph of a 60-nm thick gold film after heat treatment at 380°C.

3. Preparation and structure of the films

The silicon substrates were cleaned by the usual procedure [5] and flashed at 1300 K after insertion into the UHV cell. It was checked in a separate UHV apparatus that a 7 × 7 superstructure develops in the LEED pattern after such a treatment, and no contaminations could be detected in the Auger spectra [6]. The films of 15 nm thickness were deposited at room temperature and subsequently warmed up with a constant velocity of 4 K/min. Immediately after deposition, the gold film exhibits a homogeneous single-crystalline structure with a six-fold symmetry of the LEED pattern due to the built-in twin faults [7]. After annealing at temperatures higher than the eutectic temperature, the films coagulate and form small liquid drops of eutectic composition embedded in the silicon surface. Cooling again to room temperature leads to a solidification of the drops by simultaneous demixing. It was assured by a systematical variation of the heating velocity in the range 1–20 K/min that no kinetic retardations become effective during the heating/cooling cycles. Fig. 2 shows a typical scanning electron micrograph of a 60 nm thick gold film after heating and solidification, where the gold islands can be easily detected. Note, however, that the solid gold islands exhibit no homogeneous structure but contain portions of segregated silicon.

4. Results and discussion

First the experimental arrangement was calibrated by measuring the properties of the clean silicon substrate prior to gold deposition. An excellent agreement with literature values [8,9] was obtained in spite of the fact that no corrections for window errors were used. The adjustment of the sample was performed as described by Merkt [10].

The ellipsometric properties of the silicon substrate covered by the gold film can be described by a layer model, and the optical constants roughly correspond to the literature values of pure gold because the penetration depth of the light is of the order of film thickness [3]. For a quantitative comparison we have to take into account, however, that a certain diffusion of silicon into the gold film is to be expected even at room temperature or at 50°C which may be a more realistic temperature of the silicon substrate during deposition.

The sample has then been warmed up to 380°C which causes the film to coagulate and to form an eutectic mixture (18.6 atom.% Au [11]). Small liquid islands embedded in the silicon surface develop. If the film is cooled again to room temperature, the gold islands demix and solidify (Fig. 2). As a consequence, Δ as well as ψ steeply decrease because of the change in the electronic state of the gold. The solidification results in a drastic increase of the free electron density in the islands, and hence in a decrease of the real part of the effective dielectric constant ϵ_1 [12]. The phase transition occurs at a distinctly lower temperature than the liquidation. Hence, a characteristic hysteresis behaviour becomes evident in the temperature dependence shown in Fig. 3. Such a behaviour has also been observed for other binary systems [13] and can be traced back to the different mechanisms governing the melting/solidification process [14]. The melting/solidification cycles can be repeated several times without drastic changes in the hysteresis behaviour since the gold does not remarkably diffuse into the inner of the silicon. Note,

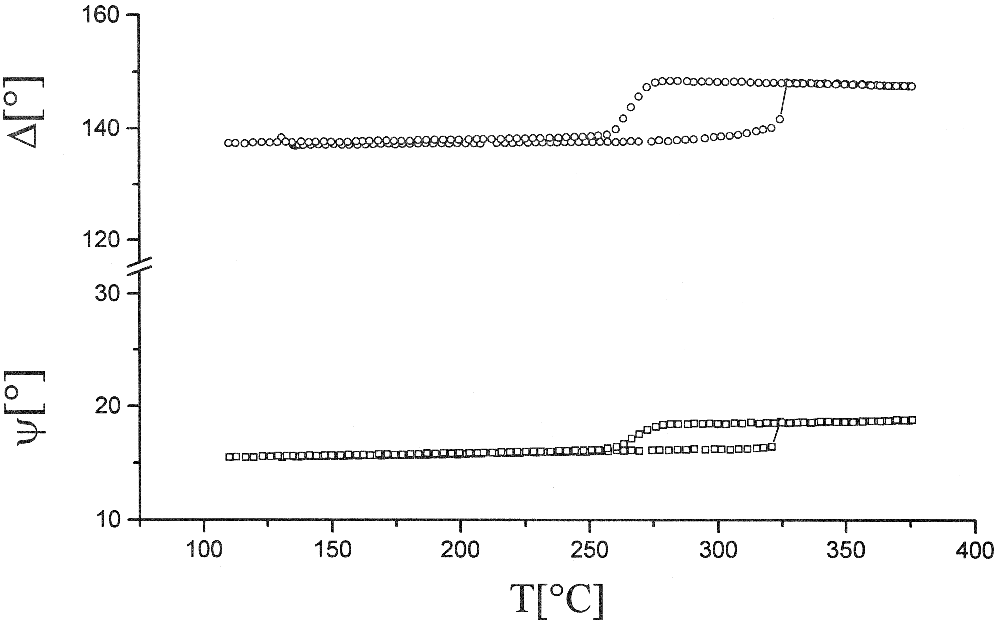

Fig. 3. The ellipsometrical angles Δ and ψ in dependence on sample temperature T ($\lambda = 500$ nm, $d = 15$ nm).

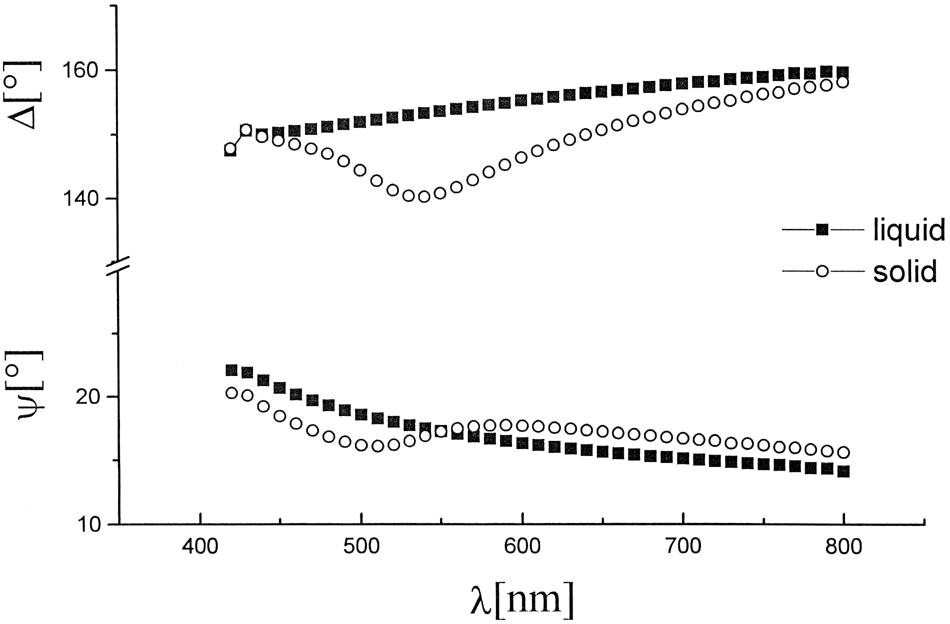

Fig. 4. The ellipsometrical angles Δ and ψ in dependence on light wavelength λ ($T = 300$°C, $d = 15$ nm).

however, that both transformation temperatures are distinctly smaller than the literature value of the eutectic temperature (363°C [11]). Similar conclusions were reported by Kato [15].

The ellipsometrical parameters of Fig. 3 were measured at 500 nm where the changes in Δ and ψ are particularly marked during the melting process. The complete wavelength dependence is shown in Fig. 4 for the solid and for the liquid state, respectively. For a discussion it seems desirable to recalculate the dielectric constants of the island layer by evaluating the data of Fig. 4 with a suitable layer model on one hand, but unfortunately reliable information on the island structure like size and shape of the islands is missing on the other hand. Hence, a consequent application of averaging procedures [16] for the optical characterization of the island layer is reserved for future work. Nevertheless, the interband transition of the gold at about 400 nm is clearly seen in the ψ vs. λ curve. In addition, a marked resonance at 570 nm develops which may be traced back to a Mie plasmon excitation in gold [17,18]. The Mie resonance disappears in the liquid state which makes the optical constants quite sensitive to the phase transition in the 500 nm wavelength regime. It should be emphasized that all these measurements on the phase transition are relative measurements on one and the same sample where the amount of gold deposited remains constant to a first approximation. Obviously, the detection sensitivity of the apparatus is quite sufficient to elucidate the influence of phase status on the optical properties.

5. Conclusions and outlook

We present a new experimental arrangement which allows in situ studies on the optical properties of Au/Si eutectic melts at various temperatures. The melting process itself shows distinct hysteresis properties due to the formation of liquid eutectic islands embedded in the silicon surface. A characteristic Mie plasmon excitation develops at 570 nm wavelength which disappears in the liquid state. We have systematically studied the dependence of these phenomena on gold film thickness and angle of incidence of the incoming light, in addition to the parameters mentioned above, i.e., temperature and light wavelength. Due to space limitations, however, we have to report on these results in a forthcoming paper [2].

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