Shapes of polarization sensitive photocurrent pulses in Ag/Pd nanocomposite films: influence of firing temperature

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Abstract. The results of investigation of the shapes of polarization-sensitive photocurrent pulses in nanocomposite Ag/Pd films with different temperatures of firing are presented. Ag/Pd nanocomposite films were produced in accordance with thick film technology at temperatures $T = 773$ and $1013$ K. Photocurrent excitation was carried out by femtosecond laser pulses. The obtained polarization photocurrent dependencies are characteristic for photocurrent due to photon drag and surface photogalvanic effects. It was shown that longitudinal photocurrent pulse duration in $773$ K films (26 ns) is significantly longer than in $1013$ K films (3 ns).

1. Introduction

It is known that silver-palladium (Ag/Pd) thick films possess temporally stable electrical characteristics and have long been used in electronics [1]. The electronic properties of the Ag/Pd films vary in a wide range depending on thermodynamics and kinetics of Pd oxidation, Ag diffusion and migration, properties of inorganic and organic additives, and other factors. These films are widely used in production of hybrid microcircuits, multicroystal modules, integrated circuit assemblies and passive electronic components [2]. Recently, it has been shown that nanosecond pulses of polarization-sensitive photocurrent depending on the direction of wave-vector can be generated in these films upon nanosecond and femtosecond laser irradiation [3,4]. According to [5,6], photocurrent generation in these films occurs in a wide wavelength range (266-3500 nm) of incident radiation due to the photon drag (PDE) [7–9] and the surface photogalvanic effects (SPGE) [10,11]. This allows one to employ the Ag/Pd films to visualize polarization of powerful laser beams by the methods described in [12,13]. Usually, the temporal shape of photocurrent generated due to the PDE and SPGE repeats the shape of a nanosecond excitation laser pulse (e.g. [14,15]), because the momentum relaxation time of charge carriers lies in the interval from $\sim10^{-12}$ to $10^{-13}$ s [16]. However, the photocurrent pulse duration in the Ag/Pd nanocomposite films is substantially longer than the duration of exciting nanosecond laser pulses [5,6]. One of the reasons for the elongation of polarization-sensitive photocurrent pulses may be the peculiarities of the electrical conductivity in these films. It is obvious that the peculiarities of electrical conductivity of the material depend on its phase composition and structure. According to [17,18], the structure, phase composition, and electrical properties of the Ag/Pd nanocomposite films essentially depend on the firing temperature. However, experiments for the investigation of the effect of the firing temperature on the pulse duration of polarization-sensitive photocurrent in these films have not yet been carried out. In this regard the purpose of this work is investigation of influence of the Ag/Pd film firing temperature on time parameters of polarization-sensitive photocurrent pulses.
2. Experimental

2.1. The Ag/Pd films
The Ag/Pd films are produced using technologies [17,19] based on firing of a special paste, which contains silver oxide (Ag₂O) and Pd, at high temperatures on the insulating substrate surface. The films studied in our experiments were fabricated at temperatures \( T = 773 \) and \( 1013 \) K from the resistive paste consisting of the following components, wt. %: Ag₂O – 24.2, Pd – 30.8, glass frit – 45 and organic binder – 25. The size of the obtained films was \( 5 \times 5 \) mm. The thickness of the films was about 10 \( \mu \)m. To measure the photocurrent, the films were provided with two parallel electrodes which were arranged along the opposite sides of the Ag/Pd film between the aluminum oxide (Al₂O₃) ceramic substrate and the film.

2.2. Photocurrent excitation
The sketches of longitudinal and transverse photocurrent measurement setups are shown in figures 1a and 1b, respectively. Longitudinal photocurrent flows in a direction parallel to the plane of incidence \( \sigma \) of laser radiation and transverse photocurrent is perpendicular to the \( \sigma \). The photocurrent was excited using femtosecond pulsed laser radiation at \( \lambda = 795 \) nm with pulse duration of \( \tau = 120 \) fs. The pulse energy was in range of 150-300 \( \mu \)J. In the experiments the linearly polarized laser radiation was directed through the quarter-wave or half-wave phase plate. The laser beam with diameter of 4 mm was passed through the phase plate and directed onto the Ag/Pd film surface at the angle of \( \alpha = 45° \).

The polarization state of the beam was determined by the angle \( \varphi \) between slow axis of the phase plate \( (n_s) \) and the polarization azimuth of the initial beam \( (x') \). When quarter-wave plate was used, the beam was left- and right-circularly polarized at \( \varphi = 45° \) and \( 135° \), respectively, and had elliptical or linear polarization at other \( \varphi \). We controlled the polarization azimuth \( \Phi = 2\varphi \) of linearly polarized incident beam by rotating the half-wave plate by the angle \( \varphi \). A digital oscilloscope with bandwidth of

![Figure 1(a, b). Sketch of the experimental setup for (a) longitudinal and (b) transverse photocurrent registration in Ag/Pd nanocomposite film: (\( \sigma \)) plane of incidence, (\( n \)) film normal, (\( k \)) wavevector, (\( x' \)) polarization azimuth of the initial beam, (\( n_s \)) slow axis of the phase plate, (\( E \)) electric field vector, (\( E, x' || \sigma \)). Electrodes are deposited on the sample’s edges (a) perpendicular and (b) parallel to the \( \sigma \), which coincides with the (xz) plane of the laboratory Cartesian frame.](image-url)
300 MHz and an input impedance of $r = 50 \, \Omega$ was used for the photocurrent registration. The energy of laser pulses ($E_{in}$) incident on the film was measured using a pyroelectric energy meter. A fast response SIR-5 $p-i-n$ photodiode (ThorLabs) with a rise time of about 60 ps connected to the same digital oscilloscope was used as a reference photoelectric converter. The temporal evolution of the photocurrent pulses was characterized by measuring the rise time and fall time, which were defined with respect to the 0.1 and 0.9 of the pulse amplitude. The duration of the photocurrent pulse was defined with respect to the 0.5 of the amplitude.

3. Experimental results and discussion
A femtosecond laser pulses produced an electric current directed parallel or perpendicular to the plane of incidence $\sigma$ (figure 1) in the film. The longitudinal and transverse photocurrents manifested themselves as an unipolar nanosecond electric pulses of voltage with extreme values $U_x$ or $U_y$, respectively.

Figure 2 shows the temporal shape of the SIR-5 photoresponse and the corresponding temporal shapes of the longitudinal (figure 2a, 2c) and transverse (figure 2b, 2d) photocurrent pulses excited in the Ag/Pd films produced at $T = 773$ K (upper oscillograms) and $T = 1013$ K (lower oscillograms). The longitudinal photocurrent was registered at $p$-polarized excitation, and the transverse one was excited by left-circularly polarized beam.

![Figure 2a-d](image)

**Figure 2(a-d).** Oscillograms of (a, c) longitudinal and (b, d) transverse photocurrent pulses induced by the femtosecond laser pulses in the Ag/Pd nanocomposite films produced at (a, b) $T = 773$ and (c, d) $1013$ K, including $p-i-n$ photodiode response oscillograms.

It can be seen from table 1 that under 120 fs pulse excitation time parameters (pulse duration and fall time) of the longitudinal and transverse photocurrent pulses are significantly different for the Ag/Pd films produced at $T = 773$ and 1013 K. Thus, for $p$-polarized radiation, the pulse duration of the longitudinal photocurrent for the films obtained at 1013 K is only 3 ns, which is almost nine times less
than in samples obtained at 773 K. It is noteworthy that the fall times of the photocurrent pulses presented in figure 2 differ from each other by a higher factor.

Table 1. Time parameters of the longitudinal and transverse photocurrent pulses in Ag/Pd films synthesized at \( T = 773 \) and 1013 K.

|                  | Rise time (ns) | Fall time (ns) | Pulse duration (ns) |
|------------------|----------------|----------------|---------------------|
|                  | 773 K          | 1013 K         | 773 K               | 1013 K             |
| Longitudinal     | 3.6            | 3.6            | 295.8               | 8.8                | 26.4               | 3             |
| Transverse       | 3.6            | 3.2            | 44.8                | 14.4               | 8.8                | 3.6           |

According to our previous studies [4], the dependence of the photocurrent in Ag/Pd films on the laser energy is linear, so it is convenient to represent the photocurrent as conversion efficiency: \( \eta_x = i_x/E_{in} \) and \( \eta_y = i_y/E_{in} \) for the longitudinal and transverse photocurrents, respectively, where \( i_x = U_x/r \) and \( i_y = U_y/r \). The photocurrent polarization dependencies for the Ag/Pd film synthesized at \( T = 1013 \) K are presented in figure 3. One can see from figure 3a that the dependence \( \eta_x(\Phi) \) is an even function, positive at all polarization azimuth values. It reaches its maximum and minimum values at s- and p-polarized laser beams, respectively, which is in good agreement with the theory of simultaneous generation of the photocurrent due to the PDE and SPGE described in [6]. The dependence \( \eta_y(\Phi) \) (see figure 3b) is an odd function, and has its zero values at p- and s-polarizations of the incident radiation and the maximums at \( \Phi = \pm 45^\circ \). By rotating the quarter-wave plate, we registered a superposition of linear and circular photocurrents [5] generated simultaneously (figure 3c). All presented polarization dependences correspond to those obtained earlier for the films produced at a lower temperature. Therefore, the photocurrent in the films produced at \( T = 1013 \) K can be considered to be generated due to PDE and SPGE mechanisms. The difference is that the conversion efficiency for those films decreased by factors of 1.4 and 1.8 compared to the films obtained at \( T = 773 \) K for s-polarized and circular polarized incident radiation, respectively.

Figure 3(a-c). (a) – longitudinal and (b) – transverse photocurrent dependences on polarization azimuth \( \Phi \), (c) – transverse photocurrent dependence on the quarter-wave plate orientation angle \( \varphi \). The red solid curves are fittings of the experimental data, the blue dashed and green dotted curves denote circular and linear contributions, respectively. Orientations of the electric field vector are shown at the top.

Figure 4 shows the X-ray diffractogram fragments of the Ag/Pd film samples obtained at different firing temperatures. Analysis of the diffractograms shows that the main components of the films in
both cases are nanocrystallites of the Ag-Pd solid solution and palladium oxide (PdO). Herewith, the Ag-Pd solid solution is represented by two phases both for low and high firing temperatures. All solid solution phases have different proportions of Ag and Pd and different parameters of the crystal lattice. Films nanocrystallite sizes are in range of 28-98 nm. With an increase in the firing temperature, the Ag-Pd peaks shift to the right, which may indicate an increase in the Pd content in the solid solution. At the same time the ratio of the heights of the peaks of PdO and Ag-Pd decreases with the increase in temperature, that is, the relative content of PdO is also reduced. Thus, it can be assumed that the additional Pd released at a higher firing temperature from the PdO passes into the solid solution. This is in agreement with previously obtained results [17].

![Diffractograms](image)

**Figure 4(a, b).** Fragments of diffractograms of the Ag/Pd nanocomposite films produced at (a) \( T = 1013 \) and (b) \( 773 \) K, and main X-ray diffraction patterns of detected phases (CuK\(_\alpha\) radiation)

It follows from the presented experimental results that the change in the phase composition of the films leads to shortening of the photocurrent pulses for the films with higher temperature of the firing. According to our previous research, Ag/Pd films have porous nanocomposite structure [17] (size of pores depends on the firing temperature [18]), formed by a mix of Ag-Pd metal and PdO semiconductor nanocrystallites in an amorphous dielectric glass matrix. Nanocrystallites of Ag-Pd solid solution and PdO act as resistors, and dielectric barriers made of amorphous glass act as capacitors, accumulating charge. Furthermore, PdO inclusions in the matrix of the film form Schottky barriers with the Ag-Pd solid solution. Thus, Ag/Pd nanocomposite can be represented as a complex system containing a set of randomly distributed RC circuits. When photocurrent is generated on the surface [4], part of it flows in short-circuits in the bulk of the sample. Charge is accumulated on the “capacitors” in the course of photocurrent generation. When the photoexcitation ends, this “capacitors” will discharge, with part of the current passing through the measuring oscilloscope, and the other part will charge adjacent RC circuits of the nanocomposite, leading to the subsequent charge...
and discharge. Therefore, charge and discharge processes, which can persist even after the end of photoexcitation, will occur in the bulk of the film. As the result, the fall time of the photocurrent pulse, registered by the oscilloscope, will be significantly higher than the relaxation time of the photoexcited electrons. Charge and discharge times depend on capacitance and resistance of the elements of RC circuits, therefore structure and composition of the Ag/Pd films influences the photocurrent pulse duration. This mechanism, presumably, is the main reason behind elongation of the PDE and SPGE photocurrent pulses in the Ag/Pd films.

4. Conclusion
The nanocomposite Ag/Pd films were produced at firing temperatures of 773 and 1013 K. The main phase components of the films are the solid solution Ag-Pd and PdO. The films produced at higher temperatures have a lower PdO content relative to the Ag-Pd. The content of Pd in the Ag-Pd solid solution increases with the increase in the firing temperature. The amplitude of the photocurrent excited by femtosecond laser pulses decreases at the same time. The nanosecond polarization-sensitive longitudinal and transverse photocurrent pulses are significantly shorter in the Ag/Pd films produced at 1013 K than in the films produced at 773 K. The research results can be used to develop and create fast response polarization-sensitive sensors based on the Ag/Pd films.

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