Application of Organosilicon Plasma Polymers in Electroluminescent Display Structures

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Abstract. Plasma polymerization is a modern and prospective method for obtaining thin dielectric films, which possess mechanical, chemical, thermal, radiation stability and good adhesion to any substrate. They are very attractive as protective and capsulating layer in electroluminescent display structures. The paper refers to synthesis of plasma polymers from hexamethyldisiloxane on the heterogeneous matrix of the emitting layer. The polymer layer of high cross-linking and branched structure and thickness < 1 μm protects the structure against electrical breakdown. More over the deposition of the same polymer as upper layer on the structure protects it from environmental conditions. The optical and photo-luminescent properties of plasma polymer layers synthesized from hexamethyldisiloxane have examined. The value of the polymer layer transparence is in the limits from 55% at 400 nm to 88% at 800 nm. The photoluminescence has stimulated by using the spectral line 365 nm emitted by an Hg spectral lamp. The result of study the new electroluminescent display structure the protective and capsulating layer of organosilicon plasma polymer has prepared by perfect technology. The structure obtained is characterized by a significant increase of the emission brightness, compared to inorganic protective layers. For electroluminescent structures with a chalcogenide, protective layer the increase is more than 6 times and for structures with heterogeneous matrix on the base of TiO_2 – more than 20 times. As a stable coating the organosilicon plasma polymer increases the lifetime of the electroluminescent structures over 15000 working hours and radiation stability (Gama-radiation) up to 0,5 Mrad. The electroluminescent display structure with presented advantages is ready for economic realization in various fields of the modern society – light information in the metropolitan, airports, auto and railway stations, dispatch points, commodity and currency exchange, banks, hospitals, hotels, technological & production lines etc.

Keywords: Plasma polymerization; Organosilicon polymers; Thin films; Electroluminescent display structure

Introduction

Plasma polymerization is known as a modern and prospective method for obtaining thin nanostructured polymer films from a simple monomer, subjected to successive fragmentation and recombination. The structure of the plasma polymers substantially differs from the conventional polymers synthesized by regularly repeating units. The plasma polymers usually have highly irregular three-dimensional branched and cross-linked network, which determines a set of useful properties of the thin films obtained. The later are dielectrics with chemical resistance, mechanical toughness, thermal stability and good adhesion on any substrate. The organosilicon plasma polymer films are of particular interest. They are applicable as protective coatings [1-3], dielectric films with good adhesive properties [4], selective gas membranes [5], gas sensors [6-9], biocompatible films [10-13], etc. More over some tests with such plasma polymers have showed that they could be very attractive as protective and capsulating layer in electroluminescent display structures [14].

The paper refers to study of thin plasma polymer films (above 1 μm) from hexamethyldisiloxane (HMDSO) synthesized on the heterogeneous matrix of the emitting layer as protective film and electroluminescent structure as capsulating coating. The optical and photo luminescent properties of plasma polymers are examined. The brightness-voltage characteristics of the electroluminescent structure obtained was investigated. Conclusions were drawn on the possibilities and advantages of the electroluminescent display structure with protective and capsulating layers of organosilicon plasma polymers.

Experimental Data

The investigated polymer layers were deposited by plasma polymerization process. The

plasma reactor system is schematically depicted (Fig. 1). The capacitively coupled glow discharge was accomplished between two horizontally aligned aluminum electrodes, positioned at a distance of 20 mm. No carrier gas was used. Hexamethyldisiloxane (> 99 % Merk) was supplied as a monomer. The gas pressure was controlled by a M301 gauge (Hochvacuum, Dresden) and by a digital voltmeter V534 (Meratronic, Poland). The plasma excitation of the monomer gas was achieved at 400 V, 50 Hz and 1.5 mA/m^2 current density. The monomer flow rate was fixed to 5.56x10^{-7} m^3/s, the gas phase pressure was 266 Pa. Glass plates and emitting layers were used as substrates of the electroluminescent structures. The polymer layer thickness estimated from the frequency shift of a mass sensitive quartz resonator before and after polymer deposition varied from 0.4 μm to 0.8 μm.

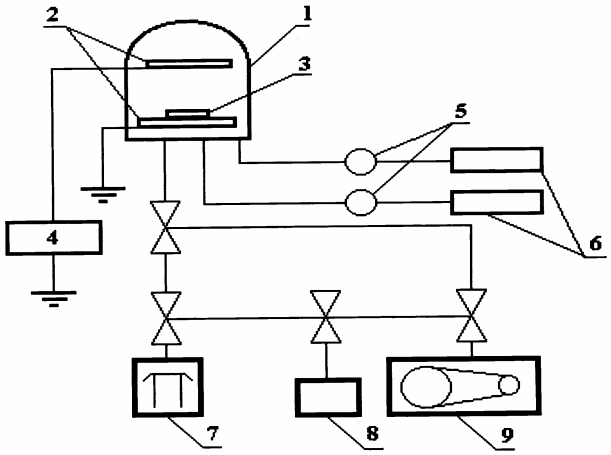

Fig. 1 *Vacuum system for synthesis of polymer layers in a glow discharge: 1 – reactor chamber; 2 – electrodes; 3 – sample holder; 4 – power generator; 5 – micro valves; 6 monomer containers; 7 – diffusion pump; 8 – vacuum balloon; and 9 rotary pump.*

As it is described above, plasma polymers are included in an alternating current hybrid electroluminescent display structure as protective and capsulating layers. A schematic diagram of hybrid electroluminescent display structure is shown (Fig. 2). Lower transparent electrode 2 of a SnO_2 layer is formed on a plane-parallel glass substrate 1. The active emitting layer 3 is prepared of industrial ZnS electroluminophores with yellow emission (electroluminescent 570 M), dispersed in one-component transparent polyepoxy oligomer used as a binder. This oligomer is characterized by a high molecular weight (4000 – 6000 mol.units), a dielectric constant $\varepsilon = 4.6$ and small dielectric losses tg $\delta = 10^{-2}$. There were not changes of dielectric properties and capacitance in wide range from 400 Hz to 20 kHz. The protective layer 4 in the investigated structure is an organosilicon plasma polymer with different thickness – from 0.4 μm to 0.8 μm. In order to compare plasma polymers to other protective layers two materials were used. The first was a heterogeneous matrix, prepared by TiO_2, dispersed in the oligomer mentioned above with a thickness of about 20 μm and the second ones was a vacuum deposited chalcogenide semiconductor by As_2S_5 with a thickness of 1.2 μm. Vacuum evaporated aluminum with purity 99,999 % was used to form the lower 5 and upper 6 electrodes. The display structure is capsulated with the same organosilicon polymer layer 7. The prepared hybrid electroluminescent structure emits light when exciting alternating sinusoidal or pulse voltage U is applied to the electrodes.

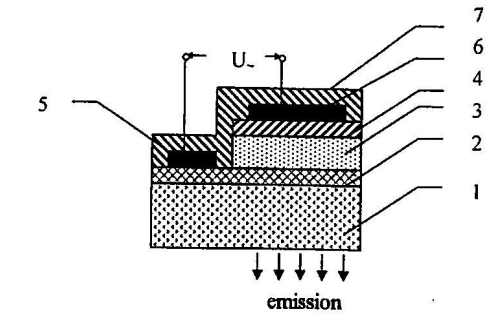

Fig. 2 *The cross-section of a AC HELDS: 1 – a plane-parallel glass substrate; 2 – a lower transparent electrode; 3 – active emitting layer; 4 – protective layer; 5,6 – aluminium electrodes; 7 – capsulating layer; U – alternating voltage.*

The plasma polymer layers are deposited onto a glass substrate in the photo-luminescent measurements. The light emission with a wavelength of λ = 365 nm of a gas discharge Hg spectral lamp illuminated the sample through an interferometric filter (K. Zeis, Germany). The photoluminescence is detected by a spectrophotometric system, comprising a monochromator DMR-2 (LOMO, Russia) – spectral range 360-800 nm, a photomultiplier (LOMO type 106, Russia) and a Lock-in Nanovoltmeter (Unipan type 232 B, Poland). The optical system is protected against both incident and reflected light beams. An entrance slit of 1 mm is chosen.

The transparence was measured by using a spectrophotometer Specord UV VIS (Germany).

The brightness values of the examined HELDS were measured by a specially constructed measuring set-up in the frequency range from 400 Hz to 1200 Hz at an excitation voltage from 50 V to 180 V.

Results and Discussion

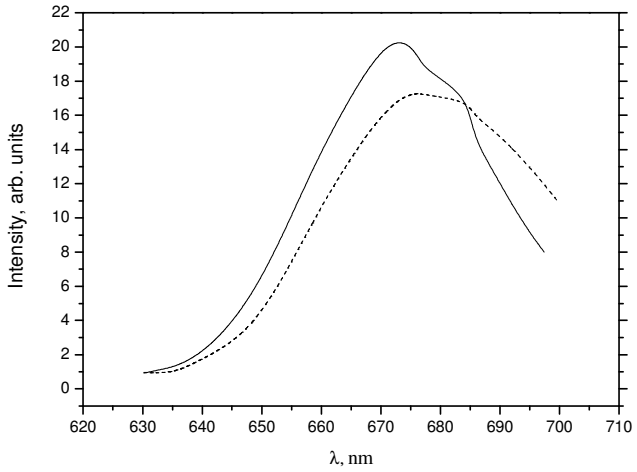

Fig. 3 *Photoluminescence spectra of plasma polymers estimated by light illumination l ¼ 365 nm with thicknesses of 0.6 μm (thick line) and 0.8μm (broken line).*

Fig. 3 illustrates the photoluminescence spectra of two polymer layers with different thicknesses. The comparison suggests a spectrum shift to the red spectral region (bato chromatic effect) when the layer thickness increases. Simultaneously, the photoluminescence intensity decreases slightly (hypo chromatic shift). This tendency is kept for layer thicknesses from 0.4 μm to 0.8 μm. These properties are observed also at light illumination with λ = 378 nm although the photoluminescence is of lower intensity here. The experimental data illustrate both the defined relation between the layer thickness and photoluminescence intensity – hyperchromatic and hips chromatic shifts (to the shorter wavelength) at smaller thickness.

The polymer layer was treated thermally at 120^0C for 20 min. This procedure packs up and stabilizes the layer. After it, the measured photoluminescence spectra turned out to be hyperchromatic and hips chromatic shifted compared to those of the annealed layer.

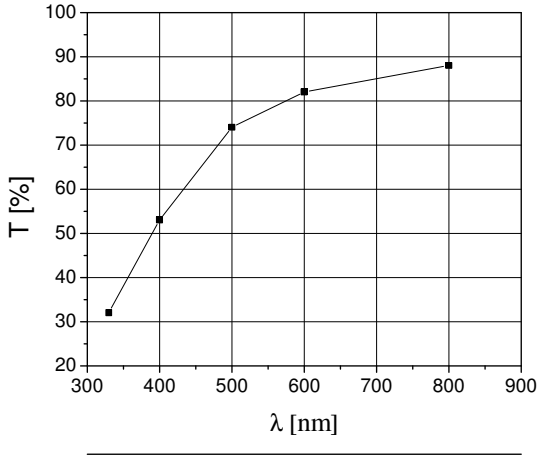

Fig. 4 *Transparence T of an organosilicon plasma polymer of 0.8μm thickness.*

The transparence (T) of the polymer layers was studied in the spectral region 330-800 nm (Fig. 4). The value of T is found to vary from 30% to 88%. The above thermal treatment does not affect the transparence T-value.

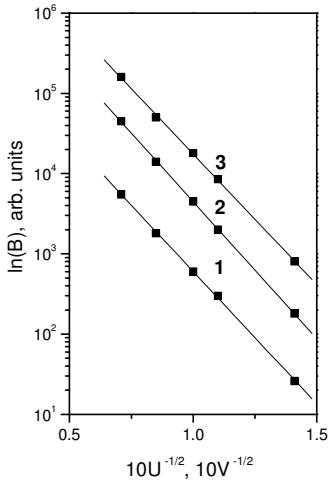

Fig. 5 The brightness B-voltage U characteristics (ln B=f($U^{-1/2}$) of the inorganic hybrid electroluminescent matrix structure of Drestiau type with yellow emission at voltage frequency 1.2 kHz and various protective layers: 1 – heterogeneous TiO_2 (20μm) ; 2 – chalcogenide As_2S_5 (1.2μm) ; 3 – organosilicon plasma polymer (0.4 μm).

The brightness B of the investigated hybrid electroluminescent display structure depends exponentially on the excitation voltage U [15]. The brightness-voltage dependence B(U) is $\ln B = f\left(1/\sqrt{U}\right)$. *The* B (U) *characteristics of the inorganic hybrid electroluminescent matrix structure of Drestiau type with yellow emission at a constant frequency (1200 Hz) and various protective layers are shown (Fig. 5).*

The electroluminescent structure is protected by a plasma polymer layer demonstrates a significant increase of the emission brightness (Fig. 5, curve 3) compared to the inorganic protective layers. For hybrid electroluminescent display structures with a chalcogenide protective layer the increase is more than 6 times (Fig. 5, curve 2) and for structures with heterogeneous matrix on the base of TiO_2 – more than 20 times (Fig. 5, curve 1). The reasons for this enhanced electroluminescent emission might be ascribed to processes accomplished at the interface "*active layer (semiconductor) – protective layer (plasma polymer)*". By an analysis of the *C*(*V)* characteristics for metal-polymethyl-siloxane-semiconductor (silicon) structures M. Maisonneuve et al. [16] established the presence of low mobility (10^{-16} cm^2 V^{-1} s^{-1}) positive ions and of higher mobility (10^{-10} cm^2 V^{-1} s^{-1}) electronic charges within the polymer layer, placed at the interface metal-polymer. Similarly, positive ions and electronic charges could be found at the interface "*electrode (metal) – polymer (dielectric)*" of the studied electroluminescent structure. In electrical field the positive ions and electrons could move to the interface polymer-semiconductor. This accumulation of charges may cause the increase of the structures brightness.

The lifetime (the time interval during which the brightness falls down to 50% of the initial value) of the structures with organosilicon plasma polymer capsulating layer is not less than 15 000 working hours.

Conclusion

New electroluminescent display structure is prepared by perfect technology, in which the protective and capsulating layer is organosilicon polymer synthesized by plasma polymerization. The structure is characterized by a significant increase of the emission brightness, compared to inorganic protective layers. The increase for electroluminescent structures with a chalcogenide protective layer is more than 6 times and for structures with heterogeneous matrix on the base of TiO_2 – more than 20 times. Other advantages of electroluminescent displays prepared based on these alternating current hybrid electroluminescent structures are:

- Flat construction and creation of small as well as wide-size displays with various form, configuration, high density of the signs on small areas. These displays can be used for representation of static and dynamic information;
- Radiation stability (γ-radiation) up to 0,5 Mad.
- High reliability (up to 1.10^{-6} 1/h);
- Life time over 15000 working hours;
- Large viewing angle ensuring observation from a wide range of angle without distortion and significant loss of brightness;

- Possibility for multi-color light emission in one and the same structure;
- Cheap technology;
- Energy – effective and ecological displays.

Possibilities of Application

The alternating current hybrid electroluminescent display structure with presented advantages is ready for economic realization:

- Widesize alternating current hybrid electroluminescent displays with different configuration –letter, digital and another signs;
- Polycolor alternating current hybrid electroluminescent structure signal board;
- Alternating current hybrid electroluminescent structure's with high brightness and stability using as protective and capsulating layers plasma polymer films.

This alternating current hybrid electroluminescent structure can be used in various field of the modern society – light information in the metropolitan, airports, auto and railway stations, dispatch points, commodity and currency exchange, banks, hospitals, hotels, technological and production lines etc.

References

1. G. **Grundmeier**, P. **Thiemann**, J. **Carpentier**, V. **Barranco**, Tailored thin plasma polymers for the corrosion protection of metals, *Surface and Coatings Technology*, **174-175**, 996-1001 (2003).
2. R. **Balkova**, J. **Zemek**, V. **Cech**, J. **Vanek**, R. **Prikryl**, XPS study of siloxane plasma polymer films, *Surface and Coatings Technology*, **174-175**, 1159-1163 (2003).
3. M. P. **Bonnar**, B. M. **Burnside**, A. **Little**, R. L. **Reuben**, J. I. B. **Wilson**, Plasma polymer films for drop wise condensation of steam, *Chemical Vapor Deposition*, **3**(4) 201-207 (2004).
4. X. **Wang**, G. **Grundmeier**, Morphology and patterning processes of thin organosilicon and perfluorinated bi-layer plasma polymer films, *Plasma Processes and Polymers*, **3**(1) 39-47 (2006).
5. N. **Inagaki**, S. **Tasaka**, H. **Abe**, Adsorption of carbon dioxide in plasma polymers prepared from silicon compounds and carbon dioxide separation membrane, *Polym. Bull*., **33**(6) 709-715 (1994).
6. E. **Radeva**, L. **Spassov**, Effect of plasma polymerization conditions on the humidity sorptive properties of thin films obtained from hexamethyldisiloxane in glow discharge, *Vacuum*, **51,** 217-220 (1998).
7. E. I. **Radeva**, I. D. **Avramov**, Humidity sensing properties of plasma polymer coated surface transverse wave resonators, *Proc. of the IEEE Ultrason. Symp.*, Sendai, Japan (1998) 509-512.
8. I. D. **Avramov**, S. **Kurosava**, M. **Rapp**, P. **Krawczak**, E. **Radeva**, Gas sensitivity comparison of polymer coated SAW and STW resonators operating at the same acoustic wave length, *IEEE Sensors journal*, 2(3) 150-159 (2002).
9. L. **Arapan**, G. **Alexieva,** I. D. **Avramov**, E. **Radeva**, V. **Strashilov**, I. **Katardjiev**, V. **Yantchev**, Highly Mass-Sensitive Thin Film Plate Acoustic Resonators (FPAR), *Sensors*, **11**, 6942-6953 (2011).
10. L. **Pramatarova**, E. **Radeva**, E. **Pecheva**, T. **Hikov**, N. **Krasteva**, R. **Dimitrova**, D. **Mitev**, P. **Montgomery**, R. **Sammons**, G. **Altankov**, The Advantages of Polymer Composites with Detonation Nanodiamond Particles for Medical Applications, *InTech*, Chapter On Biomimetics **14**, 297-320 (2011).
11. N. **Krasteva**, K. **Hristova**, E. **Radeva**, E. **Pecheva**, R. **Dimitrova**, L. **Pramatarova**, Effect of Ammonia plasma treatment on the biological performance of plasma polymerized hexamethyldisiloxane, *AIP Conf. Proc. 1203* (2010) 688-693.
12. E. **Radeva**, L. **Pramatarova**, E. **Pecheva**, T. **Hikov**, E. **Iacob**, L. **Vanzetti**, R. **Dimitrova**, N. **Krasteva**, T. **Spassov**, D. **Fingarova**, Study of organosilicon plasma polymer used in composite layers with biomedical application, *AIP Conf. Proc. 1203* (2010) 949-954.
13. P. **Favia**, R.d'**Agostino**, Plasma treatments and plasma deposition of polymers for biomedical applications, *Surface and Coatings Technology*, **98,** 1102-1106 (1998).
14. L. **Yourukova**, K. **Kolentsov**, E. **Radeva**, Effect of a second protective layer in AC EL display structures on their characteristics, *Vacuum*, **76,** 199-202 (2004).
15. I. K. **Vereschagin**, *Electroluminescent light sources*, Moscow, Energoatomizdat (1990) p. 57.
16. M. **Maisonneuve**, Y. **Segui**, A. **Bui**, Charge transport in thin polymer films as shown by $C - V$ measurements, *Thin Solid Films***, 44**(2) 209-216 (1977).