Mechanism of the luminescence of polymer films during their formation as a result of bombardment of solids with ion beams

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It was established that the luminescence of helium or neon atoms and molecules, which is observed during bombardment of metal targets with He$^+$ or Ne$^+$ ions,[1-3] is emitted by the particles of the gas in question enclosed within hollow spherulites formed during growth of polymer films on the surfaces of the bombarded targets. The influence of the film temperature on the intensity of the emitted luminescence and the influence of the nature of bombarding particles on the nature and intensity of the luminescence are explained on the basis of a proposed mechanism of the luminescence of polymer films. A mechanism is also suggested for the luminescence emitted by polymer films formed on the surfaces of dielectric targets bombarded with ion beams.

INTRODUCTION

It was reported in[1-3] that the process of formation of polymer films by bombardment of metal (Ta, Cu) or dielectric (NaCl) targets with He$^+$ or Ne$^+$ ions is accompanied by luminescence. In contrast to the luminescence of knocked-out excited target atoms[4] or the luminescence of ion beams which have experienced charge exchange after scattering from the surface of a target,[5] the luminescence discussed here does not give rise to a halo of any significant size. An analysis of the luminescence spectrum of a polymer film which is observed during bombardment of the film surface with He$^+$ or Ne$^+$ ions has demonstrated that it is emitted by the excited helium or neon atoms and molecules.

It is suggested in[2] that the luminescence of polymer films bombarded with ions is emitted by the excited helium or neon atoms and molecules knocked-out by the incident ions from the polymer film saturated with particles of these gases during the preceding ion irradiation. Later, more detailed experimental investigations of this phenomenon showed that the mechanism proposed in[2] for the luminescence of polymer films bombarded with ions cannot explain some of the new observations. On the other hand, an analysis of these observations has suggested a different mechanism of the luminescence of polymer films formed on solids as a result of dissociation, by the bombarding ions, of hydrocarbon molecules adsorbed on the target surface. The present paper is a report and discussion of experimental results which are used as the basis of a new mechanism of the luminescence mentioned above.

EXPERIMENTAL RESULTS AND DISCUSSION

The apparatus used in the bombardment of solid targets with ion beams was similar to that described in[4]. A polymer film formed as a result of simultaneous incidence, on the target surface, of an ion beam (helium or neon ions of 20 keV energy, ion current density 50–100 μA/cm^2) and a beam of hydrocarbon molecules.[1)] The luminescence spectra of the polymer films formed in this way were studied with an ISP-51 spectrograph. The luminescence spectrum in the 4000–7500 Å range was photographed on I-750 and RF-3 films. The intensity of the luminescence beam selected by the spectrograph was measured by a photoelectric unit operating under pulse counting conditions.[6] A comparison of the results of visual and spectroscopic investigations of the luminescence with the results of a morphological study of the polymer films emitting this luminescence played an important role in the determination of the luminescence mechanism. The morphological studies were carried out with a MIM-7 metallographic microscope (×450) and an UÉMV-100V electron microscope (×1000–50 000).

The process of formation of a polymer film and characteristics of the emitted luminescence were different for metal and dielectric substrates. Some of these differences can be deduced from an examination of Fig. 1 which shows photomicrographs of the surfaces of polymer films formed as a result of the bombardment of a copper ribbon (a) and a cleaved NaCl single crystal (b) with Ne$^+$ ions. The photomicrographs in Fig. 1a correspond to different intensities of the luminescence of the polymer film: microgram I shows the surface of the film at the moment when the luminescence begins to appear, microgram II is the same surface under the conditions corresponding to the maximum intensity of the luminescence, and microgram III shows the surface of the film at the time when the luminescence begins to disappear. The time intervals separating photomicrograms I, II, and III are given in Fig. 2, which shows the dependences, on the duration of irradiation, of the luminescence intensity of the Ne I line at λ = 5852 Å and of the Ne$_2$ molecular band at λ = 5400 Å. An examination of the curves in Fig. 2 shows that a strong luminescence of the polymer films appears after 1-h bombardment of the target with the ion beam; the intensity maximum is reached in about 2 h and the luminescence begins to decay after 5 h.

It is evident from microgram I in Fig. 1a that there are many small spherulites (average size 0.5 μ) on the surface at the moment when the luminescence begins to appear.[2)] The size of the spherulites increases with increasing luminescence intensity (II in Fig. 1a) and, finally, when the luminescence begins to decay, most of the spherulites break up (III in Fig. 1a).

The luminescence spectrum of a polymer film formed on the surface of a metal has the following features:
1) the atomic lines of neon are strongly broadened;[3)]
2) the luminescence spectrum includes bands which can

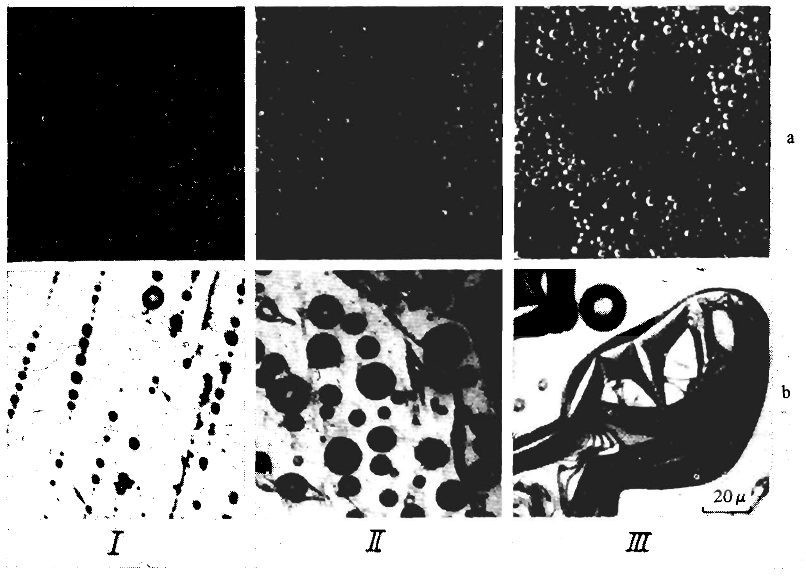

FIG. 1. Photomicrographs of the surfaces of polymer films formed on a copper ribbon (a) and on the surface of a freshly cleaved NaCl crystal (b): I—beginning of luminescence; II—maximum luminescence intensity; III—decay of luminescence.

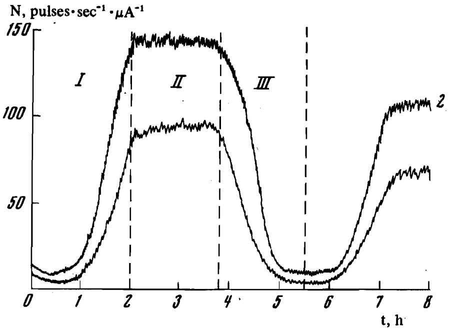

FIG. 2. Dependences of the intensity of the luminescence of neon atoms and molecules on the duration of irradiation of a polymer film formed on a copper substrate by Ne$^+$ ions: 1—atomic line Ne I, λ = 5852Å; 2—molecular band of Ne_2, λ = 5400Å.

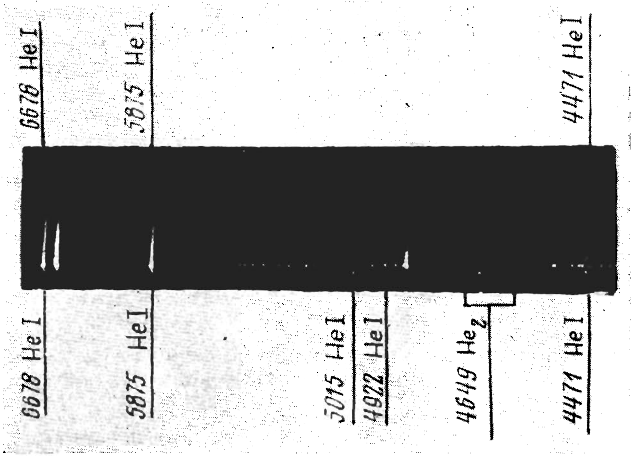

FIG. 3. Luminescence spectrum of a polymer film formed on a tantalum substrate by bombardment with He$^+$ ions.

be attributed to the emission of excited Ne_2 molecules.[3] The formation of a polymer film on a dielectric substrate is a much faster process than that observed on metal substrates. In the former case the luminescence appears approximately after 10 min from the beginning of the bombardment of the substrate with ions and the luminescence begins to disappear after 20–25 min.

A film formed on the surface of an NaCl crystal not only emits different luminescence but has a different structure. In the initial stage of the formation of such a film (I in Fig. 1b) some parts of the film do not adhere to the substrate but form cupola-like bubbles 1–5 μ in diameter. During the strong luminescence stage the diameter of these bubbles increases considerably (20–70 μ) as shown in Fig. 1b (II). During the luminescence decay stage the bubbles break up (III in Fig. 1b).$^{4)}$ One must add also that the luminescence spectrum of the films formed on the surface of NaCl consists only of the Ne I atomic lines whose width is the same as in the spectrum of the emission from a neon discharge.

Before drawing any conclusions from a comparison of the photomicrographs given in Fig. 1 with the characteristics of the luminescence of a polymer film, we must first consider the luminescence spectrum of a film formed on a tantalum substrate as a result of bombardment of its surface with He$^+$ ions (Fig. 3). The spectrum shown in Fig. 3 is recorded at right-angles to the plane formed by the axis of the bombarding beam and the normal to the target surface. It is evident from this figure that the luminescence spectrum includes broadened helium lines (λ = 6678, 5875, 4471 Å) which are emitted by the fast excited helium atoms generated by neutralization and excitation of the incident He$^+$ ions during their scattering from the target surface.[5] The intensity of these helium lines decreases with height, i.e., with the distance of the departing excited helium atom from the target surface, since the number of excited helium atoms in the scattered beam decreases as a result of emission of light. For this reason the upper edges of the spectral lines are not sharp.

Apart from the aforementioned helium lines, the luminescence spectrum of this polymer includes also short helium lines and bands (lines λ = 6678, 5875, 5015, 4922, 4471 Å and a band at λ = 4649 Å, located below the reference spectrum) with sharply defined upper edges. This feature of the short spectral lines in the luminescence spectrum of a polymer film suggests that the lines cannot be emitted by excited particles departing from the film surface.

If we utilize all the reported experimental observations, we can suggest a new mechanism of the luminescence polymer films which differs basically from that proposed in[2]. This mechanism is different for polymer films formed on metal and dielectric substrates and, therefore, these two cases will be considered separately.

We shall start by discussing the mechanism of the luminescence of polymer films formed on metal substrates. The photomicrographs in Fig. 1a demonstrate convincingly that the luminescence is due to the spherulites formed during growth of the polymer film. No luminescence is observed in those cases when these spherulites are absent from the surface of the film. When they are destroyed, the luminescence disappears.

The spherulites observed on the surface of a polymer film are the products of the spherulitic crystallization of the polymer.5) Thus, there are grounds for asserting that the crystalline spherulites formed in the course of growth of a polymer film are the source of the investigated luminescence.6) However, no further progress can be made without considering why a spherulite bombarded with ions emits luminescence.

We can suggest three mechanisms for the luminescence of a spherulite during ion bombardment. The first is formulated in[2] and it is based on the assumption that the luminescence in question is emitted by excited helium or neon atoms and molecules knocked out by the bombarding beam ions from the surface of a spherulite which has become saturated with helium or neon particles during the preceding ion irradiation. This mechanism must be rejected because it fails to explain why the spectral lines of the luminescence emitted by the spherulites have sharply defined upper edges (Fig. 3).

We may also assume that the observed luminescence is emitted by the excited beam particles implanted into the spherulites. However, this assumption is unlikely to be correct because the implanted inert-gas atoms are unlikely to form molecules inside the spherulites and thus give rise to the molecular bands observed in the spectra. Moreover, it is well known[8] that the energy spectrum of a particle implanted into a solid matrix is quite different from the spectrum of a free particle and, therefore, this should alter the emission wavelengths of the implanted particles. This effect was not observed in the present study although it would have been easily noticeable with the aid of the spectroscopic apparatus used in our study of the luminescence spectra of the polymer films.

We shall demonstrate later that the most likely mechanism that can explain the emission of luminescence by spherulites is based on the assumption that in the course of formation of a polymer film a spherulite becomes filled, because of continuous dissociation of the adsorbed hydrocarbon molecules by the incident ions, with the gas of the same nature as the particles in the beam used later. The observed luminescence can be explained by the presence of gas-filled spherulites only if the walls of such spherulites are sufficiently thin to permit penetration of the bombarding particles and to allow the escape of the photons emitted by the excited gas particles inside the spherulite. These two conditions can be quite easily satisfied if the spherulite walls are of the order of several hundred angstroms. The hypothesis of the formation of gas-filled spherulites is not as exotic as it would seem at first sight. It is well known that gas bubbles form in metals which are bombarded with ion beams.[9] The radii of these bubbles can reach values of the order of hundreds of angstroms. The properties of our polymers are such that the strength of the thin spherulite walls should be sufficient to withstand the pressure of the gas inside the spherulites. However, these general considerations cannot be regarded as proof of the correctness of the proposed model. In view of this, we carried out an electron-microscopic investigation of the polymer films which confirm directly the hypothesis of the formation of gas-filled spherulites.

The formation of gas-filled spherulites is demonstrated most clearly by the electron micrograph reproduced in Fig. 4. This micrograph represents a part of a polymer film formed as a result of irradiation of a copper ribbon with Ne^+ ions. A small number of fractured spherulites is observed on the surface of this ribbon. It is clear from Fig. 4 that these fractured spherulites are empty. An estimate of the thickness of the spherulites walls, deduced from the electron micrographs, gives values of the order of 100–400 Å. Thus, these walls are sufficiently thin for the penetration of the bombarding ions (the range of the 20 keV He^+ and Ne^+ ions in carbon is 2400 Å, respectively) and for the escape of the quanta of visible light (λ = 4000–7000 Å) emitted by the gas particles inside the spherulites.

Thus, it follows from our discussion that the luminescence of polymer films formed on a metal substrate can be explained by the emission of light by the particles of a gas enclosed in spherulites and excited by collision with particles of the bombarding beam which penetrate into the spherulites. However, this explanation does not hold for films formed on an NaCl crystal because the concentration of the spherulites on the surfaces of such films is insufficiently high. The luminescence spectra of the films formed on dielectric substrates consist of atomic lines of normal width (this point was mentioned earlier) and are evidently due to the excitation of the gas in the copula-like bubbles (II in Fig. 1b) by the incident ions penetrating across the thin walls of these bubbles. The absence of the molecular bands and broadened atomic lines indicates that the gas in the bubbles is at a lower pressure7) than the gas inside the spherulites.

The model of gas-filled spherulites can explain quite naturally all the experimental observations mentioned in[2]. Moreover, the same model accounts easily for some of the new observations mentioned earlier in the present paper.

For example, we can explain the dependences of the intensities of the atomic and molecular emission of neon on the temperature of the polymer film (Fig. 5). The intensities of the atomic lines (curve 1 in Fig. 5) were not greatly affected by the heating of a film to 100°C, but such heating reduced strongly the molecular bands of Ne_2^*.8) Cooling of the film to room temperature restored the luminescence intensities of the Ne atoms and the Ne_2

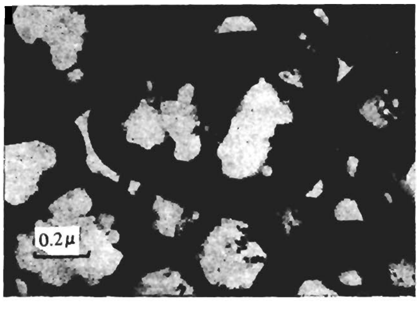

FIG. 4. Electron microgram of a polymer film formed by Ne^+ ions on a copper substrate (X50 000).

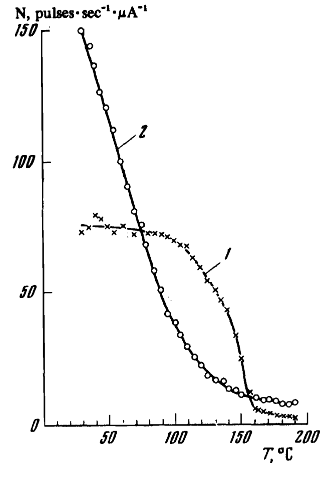

FIG. 5. Dependences of the intensity of the luminescence of neon atoms and molecules on the temperature of the polymer film: 1—atomic line Ne I λ = 5852Å; 2—molecular band of Ne_2, λ = 5400Å.

molecules observed before heating. However, the intensities of the atomic and molecular lines and bands decreased to the background level when the film was heated to 200°C. In this case cooling failed to restore the initial intensities of the lines and bands. Obviously, the reduction in the intensity of the luminescence as a result of heating to temperatures exceeding 100°C caused the escape of some of the gas inside the spherulites by diffusion across the walls.

The gas-filled spherulite model explains well the results of experiments in which the bombarding beam is changed. If a polymer film is formed by the bombardment of a target with a beam of Ne^+ ions, which emits strong luminescence of the neon particles, and then the Ne^+ beam is replaced with an He^+ beam, a neon luminescence of decreasing intensity is observed for a long time (Fig. 6a). If, after reaching a high level of the neon luminescence, the Ne^+ ion beam is replaced with an N^+ beam, the intensity of the neon luminescence (Fig. 6a) decreases to a negligible value in a much shorter time. These experimental observations can be explained as follows.

Irradiation of a target with Ne^+ ions produce a polymer film with a large number of neon-filled spherulites which are responsible for the strong emission of luminescence from the neon particles. When the Ne^+ ion beam is replaced with a beam of He^+ ions of the same energy, the nature of the processes resulting from the ion bombardment of the film changes. These changes occur because, 1) the helium ions have a larger range in the film than the Ne^+ and N^+ ions; 2) the rate of growth of the film during bombardment with the He^+ ions is much slower than during the bombardment with the heavier ions. Consequently, for a long time the walls of the spherulites remain sufficiently thin for the penetration of the He^+ ions and the excitation of the neon gas enclosed in the spherulites. The bombardment with the N^+ ions increases the rate of growth of the film and reduces the range of the bombarding ions, i.e., after a relatively short time the walls of the spherulites are too thick for the penetration of the N^+ ions.

In a different experimental setup a target was bombarded with a beam of He^+ ions, which produced a strong luminescence of helium particles, and then bombarded with a beam of Ne^+ ions, which caused a rapid fall of the intensity of the helium luminescence which eventually was replaced by the luminescence of neon particles (Fig. 6b). These experimental results can be explained by postulating that because of the high rate of growth of polymer film during bombardment with the Ne^+ ions, the helium-filled spherulites are buried under the layers of the growing film and new spherulites, which are now filled with neon, are formed in the top layers.

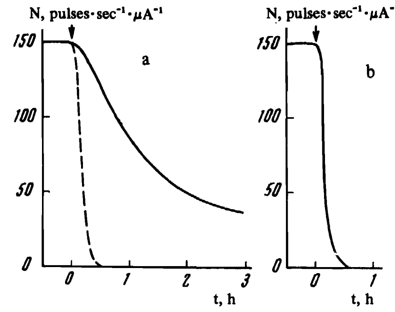

FIG. 6. Dependences of the intensity of the luminescence emitted by polymer films on the duration of irradiation with ion beams. a—Polymer film formed by bombardment with Ne^+ ions. At the moment indicated by the arrow the Ne^+ beam is replaced with a beam of He^+ or N^+ ions. The continuous curve represents the results obtained by bombardment with He^+ ions and the dashed curve is the result of bambardment with N^+ ions. b—Polymer film formed by bombardment with He^+ ions. At the moment indicated by the arrow the He^+ beam is replaced with a beam of Ne^+ ions.

The emission of luminescence by gas-filled spherulites can also explain easily the observed periodic variation of the intensity of the luminescence emitted by neon particles during continuous bombardment of polymer film with Ne^+ ions (Fig. 2). Obviously the gas-filled spherulites have a certain critical size above which they begin to break up (III in Fig. 1a). This breakup of the critical-size spherulites explains also the decay of the luminescence of the neon particles after the first maximum in the dependences N(t) in Fig. 2. The second peak of the neon luminescence intensity and its subsequent fall can be attributed to the creation of new gas-filled spherulites and their subsequent breakup.

Thus, the proposed model of gas-filled spherulites explains satisfactorily all the experimental results obtained in studies of the luminescence of polymer films formed by ion beams on metal substrates. The luminescence of polymer films formed on dielectrics is of different origin. It is likely that this luminescence is due to the excitation of the gas accumulated in cavities in the substrate and the loosely bonded polymer film.

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[1] In the formation of a polymer film by the Ne^+ ions we used a beam of VM-4 oil molecules. In the case of the He^+ ions a polymer film formed as a result of dissociation of hydrocarbon molecules present in the residual gas in the target chamber.

[2] Photomicrographs of the polymer film before the appearance of luminescence shows that the spherulites easily distinguishable in Fig. 1a (I) are not observed.

[3] The causes of the broadening of the Ne I atomic lines will be considered in a separate communication.

[4] A film formed on a dielectric substrate consists of, apart from the bubbles, a few spherulites of small radius of the same type as observed on the surface of the film formed on a metal substrate.

[5] The spherulitic crystallization of polymers is a well-known phenomenon. [7]

[6] Our electron-diffraction studies demonstrated that the spherulites formed in the course of growth of a polymer film have a crystalline structure. The results of these studies will be published in a separate paper.

[7] According to [10-12], molecular spectra and atomic spectra with broadened lines are emitted by gas discharges provided the gas pressure is sufficiently high (10-100 mm Hg).

[8] The reduction in the intensity of the emission of the excited Ne_2 molecules with increasing temperature of the film may be explained by a

shift of the equilibrium in the processes governing concentration of the $Ne_2^* + Ne + Ne \rightleftharpoons Ne_2^* + Ne$) in the gas filling the spherulites so that the predominant reaction is the dissociation of the molecules into atomic particles.

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22