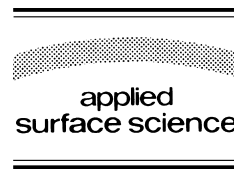




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Condensation coefficients and initial stages of growth for noble metals deposited onto chemically different polymer surfaces

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Abstract

The initial stages of growth of noble metals deposited onto untreated as well as Ar⁺ beam-treated polymer surfaces were investigated by means of X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and radiotracer methods. Condensation coefficients C of the metals on the polymer surfaces were determined by comparison of the XPS signals of the metals with the nominal thicknesses measured by a quartz microbalance during deposition. These measurements were combined with radiotracer measurements, which allow to determine C independently with high accuracy and sensitivity. C was found to depend strongly on the chemical composition of the polymer surface, e.g., at room temperature, C varies between 0.95 for PMDA-ODA polyimide and 0.002 for Teflon AF. By ion beam treatment of the latter, C was raised considerably. During nucleation of the metal on the polymer surface, C increases strongly with metal coverage. C also depends on the deposition rate of the metal and decreases strongly at elevated temperatures. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metallization of polymers is of considerable technological importance and is also of interest from a fundamental point of view (see, e.g., Ref. [1]). In general, the properties of a metal/polymer interface are determined by the interaction between the metal and the polymer and by the morphology of the interface. The interaction between moderate reactive metals (in particular noble metals) and polymers is very weak in comparison to the strong metal–metal bonding. As a consequence, such metals do not wet

untreated polymer surfaces and form clusters on it (for a review, see e.g., Ref. [2]). One way to gain further insight into metal/polymer interaction for noble metals is to determine the condensation coefficient as a function of the deposition parameters in connection with an investigation of the growth of the metals at an early stage.

The condensation coefficient C is defined as the ratio of the number of adsorbed atoms to the total number of atoms arriving at the surface. If metal atoms impinge on a clean metal surface, their condensation coefficient is generally close to unity. Little is known, however, about the condensation coefficient of metal atoms on polymers. Although many investigations of the nucleation behaviour of noble

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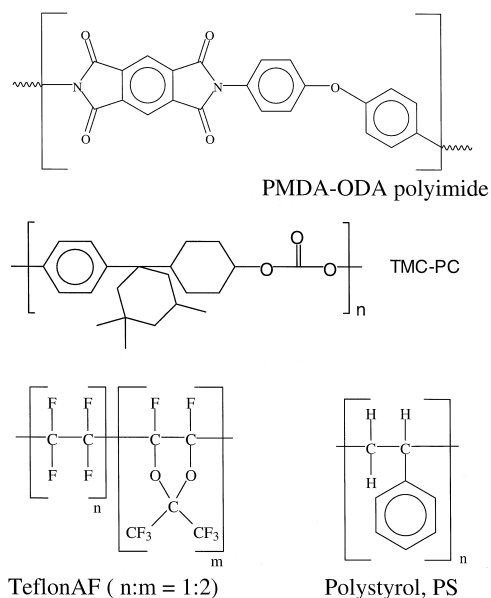


Fig. 1. Structure formula of the polymers used as substrates.

metals on different dielectric substrates were performed, only very little work has been done for polymer surfaces.

One aim of this work is to correlate the morphological properties of thin films in the early stages of the deposition process with the value of the condensation coefficient for Cu, Ag and Au on amorphous polymers substrates with different chemical compositions. The polymers shown in Fig. 1 can be distinguished by their functional groups. Both pyromellitic dianhydride-oxydianiline (PMDA-ODA) polyimide and bisphenol-trimethyl cyclohexane polycarbonate (TMC-PC) contain carbonyl groups and substituted benzene ring systems, but only polyimide contains

nitrogen also. Polystyrene (PS) has no carbonyl groups, but substituted benzene ring systems, and Teflon AF has no carbonyl groups and no aromatic systems, but a large fluorine content. Besides their chemical differences, these polymers also show different surface energies and different glass transition temperatures (Table 1). Another goal is to determine whether nucleation takes place on the free surface or at defect sites. For the systematic investigation of the morphology during the initial stages of the metal-polymer interface formation under a variety of conditions, a combination of X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and atomic force microscopy (AFM) was used.

2. Experimental

The polymer films were prepared by spin-coating or casting from solution. Thin, electron-transparent substrate films of the polymers were prepared using different methods. TEM meshes covered with a 10 nm amorphous carbon (a-C) layer were covered with a 15 nm thick PMDA/ODA polyimide film by vapour deposition or with a thin Teflon AF film by dipping into a diluted polymer solution. Transparent TMC-polycarbonate films were obtained by cutting a thick TMC-PC film with the help of an ultramicrotome. All polymer films were cured a few hours in ultrahigh vacuum (UHV) at a temperature close to their T_g before the deposition of the metals.

The metals were evaporated from a heated alumina crucible mounted in the preparation chamber of the XPS spectrometer (Omicron Full Lab). The de-

Table 1

Condensation coefficients C for noble metals on polymers at room temperature (deposition rate $R = 0.1 \text{ nm min}^{-1}$; nominal coverage $H_{\text{nom}} = Rt = 0.05\text{--}0.1 \text{ nm}$)

	PMDA/ODA polyimide	TMC-polycarbonate	Polystyrene	Teflon AF
Condensation coefficient of Ag	0.95(5)	0.12(2)	0.11(2)	0.002(1)
Condensation coefficient of Au	0.95(5)	0.27(3)	0.24(3)	0.006(2)
Condensation coefficient of Cu	0.95(5)	0.73(5)	0.26(4)	0.02(1)
Surface energy (mN m^{-1})	54.9 [8]	(45) ^a [9]	40.7 [8]	15.7 [10]
T_g ($^{\circ}\text{C}$)	≈ 420	235	100	160

^a Value is for poly(bisphenol carbonate) and is therefore only a rough estimate. Surface energies and glass transition temperatures are included for comparison.

position rate R and the nominal thickness $H_{\text{nom}} = Rt$ were monitored by a quartz crystal microbalance, which was calibrated gravimetrically. The XPS peak areas used to determine the condensation coefficients were determined after a Shirley-type background removal using the pre-installed SPECTRA software.

Micrographs were taken with a TEM (Philips CM 30) at an accelerating voltage of 200 kV. Bright-field pictures obtained with a CCD camera were edited subsequently with standard graphic software. Using phase contrast particles larger than about 1 nm can be resolved.

3. Results and discussion

3.1. Condensation coefficients for metal atoms on polymers

TEM and AFM measurements showed that the evaporated metals initially form on all polymer substrates a discontinuous layer consisting of three-dimensional spherical clusters, whose density and size depends on the deposition parameters as well as on the particular metal/polymer combination [3]. Typical micrographs for Ag, Cu and Au on PMDA/ODA polyimide are shown in Fig. 2.

As mentioned above, the condensation coefficient C is defined as the ratio of the number of adsorbed atoms to the total number of atoms arriving at the surface. Venables et al. [4] distinguished between the instantaneous condensation coefficient $\beta(t)$, which is defined as the ratio of the number of adsorbed atoms per unit time to the deposition rate, and the integrated condensation coefficient C . We have recently developed two methods to determine both parameters: a very sensitive radiotracer method to measure C [5] and XPS combined with a mathematical correction of the intensity for cluster formation to determine C and β [3]. Both will be described in detail elsewhere. In the radiotracer method [5], a radioactive metal isotope is evaporated onto a polymer sample through an aperture and the reemitted atoms are collected on a catcher foil. Using a well-calibrated system, this method allows to measure the fractions of the condensed and reemitted atoms with a high accuracy of $\pm 2\%$.

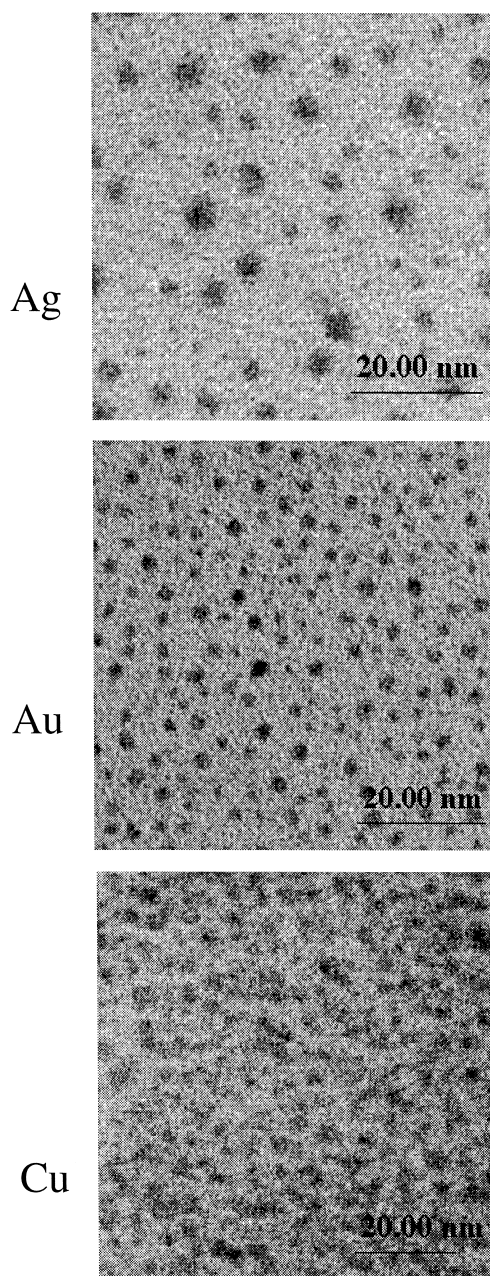


Fig. 2. Top view: TEM micrographs showing the difference in the cluster density of Ag, Au and Cu deposited on the polyimide substrate at room temperature (deposition rate 0.1 nm min^{-1} , nominal coverage 0.2 nm).

For the XPS measurements, intensities were calibrated by depositing metals onto substrates where the condensation coefficient was known to be very

close to unity, i.e., clean metal substrates or polyimide at room temperature. Below about 0.1 nm nominal coverage, the increase of the XPS intensity turned out to be a good linear approximation with coverage. Determination of C for Ag on different polymer substrates by the radiotracer and by the XPS method have shown a good agreement between the two methods, supporting the validity of the XPS results [3,5].

To better account for the effect of inelastic scattering of photoelectrons on the XPS intensity at higher coverages, spherical metal particles on a solid substrate were assumed to calculate the amount of the deposited metal [3]. As mentioned above, spherical clusters were also observed in TEM and cross-sectional TEM measurements. The validity of this method was checked using diameters of metal particles obtained directly from TEM micrographs [3]. A good agreement between XPS- and TEM-determined cluster sizes was found in all cases.

It was observed that there are two modes of condensation at RT : ‘complete’ condensation with $C \approx 1$ was seen for noble metals on polyimide, and ‘incomplete’ condensation was found for the other three polymers. Condensation coefficients for noble metals deposited onto different polymers at RT are summarised in Table 1.

A large variation is observed for the polymers, a smaller one for the metals. Apparently, differences in surface energy and/or chemical reactivity of the polymers play a major role and need to be investigated more closely in future studies.

3.2. Nucleation and growth of metal clusters

A series of experiments was performed to examine the evolution of the clusters as a function of coverage. Gold was deposited onto polyimide at room temperature (e.g., see Fig. 2), and the dependence of the cluster number density N_c on the nominal thickness H_{nom} was followed. Starting at low gold coverages, N_c increases with equivalent thickness to a maximum cluster density N_{max} at H_{nom} between 0.1 and 0.2 nm. At higher coverages, N_c decreases due to coalescence.

In the analysis of the early stages of growth, it is often difficult to distinguish between random nucle-

ation and preferred nucleation at defect sites. Within the framework of nucleation theory, this is easily accomplished by examining the dependence of the maximum number of nuclei N_{max} on the deposition rate R [6]. For polyimide, the maximum cluster density at room temperature changes with $N_{\text{max}} \sim R^{1/3.5}$ when the deposition rate R is varied in the range between 0.01–0.5 nm min⁻¹. This result supports random nucleation of the noble metals on polyimide with a critical cluster size $i = 1$, i.e., minimal stable clusters are dimers. This leads to the following temperature dependence for N_{max} [6]:

$$N_{\text{max}} \propto (R/\nu)^{1/3.5} \exp((E_d/kT)/3.5) \\ \propto (R/D_s)^{1/3.5}$$

where ν is atomic vibration frequency, E_d is the activation energy of surface diffusion, and D_s is the surface diffusion coefficient. Note that diffusion of single metal atoms into the bulk was estimated to be negligible [2]. Based on this expression, it is possible to estimate E_d for Ag by measuring the dependence of N_{max} from the substrate temperature. As can be seen in Fig. 3, the maximum cluster density can reasonably well be described by an Arrhenius-type behaviour in the temperature range where $C \approx 1$ with a diffusion energy $E_d \approx 0.08$ eV.

From the clusters density N_{max} observed in TEM micrographs, it is possible to estimate relative surface diffusion coefficients D_s for Ag, Au and Cu on

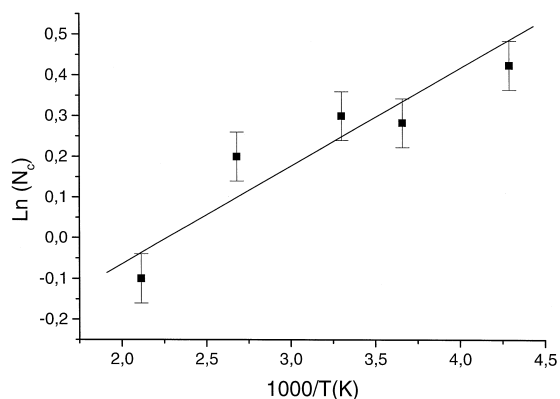


Fig. 3. Arrhenius plot of the maximum cluster density N_{max} of silver on polyimide. The deposition rate was 0.1 nm min⁻¹. The solid line is a linear least-square fit corresponding to an activation energy for surface diffusion $E_d = 0.08$ eV.

polyimide using the expression given above. Relative diffusion coefficients D_s behave like 100:2:1 for Ag:Cu:Au. This behaviour is unexpected judging from metal reactivity.

Different from polyimide, incomplete condensation occurs on the other polymers at the early stage of metal deposition. According to a model developed by Venables [6], it is possible to distinguish two basic growth modes: a steady-state regime ‘ssr’ and an aggregation regime ‘agr’. At ssr, once some stable cluster have formed an additional channel becomes important for the loss of single adatoms besides desorption, namely diffusive capture by stable clusters. The growth process is dominated by surface diffusion. The condensation coefficient for incomplete condensation is small at first, but increases rapidly with increasing cluster density. At maximum cluster density, it reaches a saturation value if the rms displacement of the adatom from the arrival site, i.e., the surface diffusion length is smaller than the distance between two clusters. In the agr mode at higher coverages, ‘direct impinging’ of atoms onto the clusters plays a role, and in this regime C increases continuously up to 1.

The morphology of the films and the condensation coefficients are correlated through the nucleation of the metal. The larger the number of nucleation sites N_c , i.e., the smaller the average distance of the growing clusters, the larger is C since the condensation is controlled by surface diffusion. By examining the dependence of the maximum number of growing clusters N_{\max} (cf. above) or of the condensation coefficient on the deposition rate R , it is possible to distinguish between random nucleation and preferred nucleation at defect sites [7]. In contrast to the condensation on PI, no dependence on the deposition rate of C and N_{\max} was observed for the other metal/polymer systems investigated. This re-

sult indicates that the nucleation at defects existing on the polymer surface plays a dominant role in the nucleation process of the metals. This can only be the case when the defects are the only deep traps compared to thermal energy. To provide further evidence that the condensation coefficient C is closely related to the defect density on the surface, a defined concentration of point defects was created by ion bombardment of the polymers using small doses of 5 kV Ar^+ ions. Even for the lowest doses used, i.e., $\approx 10^{11} \text{ cm}^{-2}$ (that is several orders of magnitude lower than the metal monolayer density of $\approx 10^{15} \text{ atoms cm}^{-2}$), the condensation coefficient increases appreciably for Ag deposition on TMC polycarbonate (from 0.12 to 0.25) and Au deposition on Teflon AF (from 0.002 to 0.008). For Au on Teflon AF an almost linear increase of C with the ion dose was observed. This behaviour can be explained with an increase of the nucleation density as confirmed in TEM measurements.

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