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RESEARCH ARTICLE

**An ethical committee approval and/or legal/special permission has not been required within the scope of this study.*

SPECTROSCOPIC INVESTIGATION OF ARGON DC GLOW DISCHARGE IN PLASMA MEDIUM

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ABSTRACT

In this study, UV-VIS-NIR (Ultraviolet Visible Near-Infrared) spectra emitted from Argon Glow discharge plasma in a low vacuum were recorded with a high-resolution Czerny-Turner type spectrometer. Argon plasma was produced at a pressure of 5mTorr and with a voltage of 584 V. Argon plasma was produced between two parallel stainless steel plates anode and cathode with a diameter of 15 cm, a thickness of 0.8 cm, and a distance of 13 cm between them. The radiative and collisional processes of the Argon plasma medium were modeled by the PrismSPECT atomic physics software (Software). The distributions of ion densities were calculated using the Saha-Boltzmann equation. The intensity of the excited energy levels of Ar(I) and Ar (II) ions were calculated in the electron temperature range of (0.4-3.5eV) and the mass density of (10^{-4}-10^{-1}gr/cm^3). *The UV-Visible-NIR spectra were simulated and compared with experimental spectra. The ratios of the intensities of the ArII/ArI* ($1s^2 2s^2 2p^6 3s^2 3p^4 4f^1 / 1s^2 2s^2 2p^6 3s^2 3p^5 4p^1$) *spectral lines were obtained for different plasma temperatures and densities. The temperature of the argon plasma was obtained from the spectral line intensity ratios.*

Keywords: *Argon glow discharge plasma, Saha-Boltzmann equation, Prismspect atomic physics software.*

Esra OKUMUŞ

PLAZMA ORTAMINDA ARGON DC GLOW DEŞARJININ SPEKTROSKOPİK İNCELENMESİ

ÖZ

Bu çalışmada, düşük vakum ortamında Argon plazmasından yayılan UV-VIS-NIR (Morötesi-Görünür-Yakın Kızılaltı) spektrumları, yüksek çözünürlüklü bir Czerny-Turner tipi spektrometre ile kaydedilmiştir. Argon plazması, 5 mTorr basınç ve 584 V voltaj parametreleri kullanılarak elde edilmiştir. Argon plazması, 15 cm çapında, 0.8 cm kalınlığında ve aralarında 13 cm mesafe bulunan iki paralel paslanmaz çelik levha anot ve katot arasında üretilmiştir. Argon Glow discharge plazmasının ışınımsal ve çarpışma süreçleri, PrismSPECT atomic physics yazılımı ile modellendi. Ar(I) ve Ar(II) iyonlarının uyarılmış enerji seviyelerinin yoğunlukları, elektron sıcaklık aralığı (0.4-3.5eV) ve kütle yoğunluk aralıkları (10^{-4}-10^{-1}gr/cm^3) seçilerek Saha-Boltzmann denklemi aracılığıyla hesaplandı. UV-Visible-NIR spektrumları PrismSPECT atomic physics yazılımı ile modellendi ve deneysel spektrumlar ile karşılaştırıldı. ArII/ArI ($1s^22s^22p^63s^23p^44f^1/1s^22s^22p^63s^23p^54p^1$) spektral çizgi yoğunluk oranı farklı plazma sıcaklıkları ve yoğunlukları için elde edildi. Argon plazmasının sıcaklığı, PrismSPECT atomic physics yazılımı ile modellenen spektroskopik çizgi yoğunluk oranlarından yaklaşık olarak elde edildi.

Anahtar Kelimeler: *Argon glow discharge plazma, Saha-Boltzmann denklemi, PrismSPECT atomic physics yazılımı.*

1. INTRODUCTION

The increase in the application of non-thermal plasma in various fields attracts the attention of researchers. The state of ionized plasma makes it different from normal gas. Laboratory plasmas are passed through a discharge tube where an electric current ionizes the gas (Braithwaite, 2000). The understanding of glowing discharge plasmas of pure or mixed gases is very important for industrial and medical applications (Stankov, Petković, Marković, Stamenković & Jovanović (2015). Several applications include the use of chemical energy through active species in the surface treatment of thin film deposition (Rafatov, Akbar & Bilikmen, 2007), microelectronics (Jung, Chi, Hwang, Moon, Lee, 1999), sterilization (Park, Lee and Park, 2003), volumetric treatment of waste separation, pollution control (Amouroux, Morvan, Morel and Martin, 2004), and biomedical applications (Florian, Merbahi, Wattieaux and Yousf, 2015). Optical methods such as emission, absorption, and laser scattering are proven techniques and methods to probe plasma environments without degrading the state and composition of the plasma (Bouchikhi, Hamid, 2010). Among these techniques, optical emission spectroscopy is widely used (Sahu, Jin & Han, 2017). This technique is based on the measurement of optical radiation emitted from the plasma, as it gives information about the properties of the plasma in the immediate environment of atomic, molecular, and ionic radiators (Bings, Bogaerts & Broekaert, 2008).

In this paper, DC glow Discharge Argon plasma is generated under vacuum and emission from plasma is studied using high resolution UV-Visible-NIR spectrometer. Argon plasma media are widely used in thin film coatings. In this study, using the spectra emitted from the plasma medium occurring between the anode and cathode which are 15 cm diameter metal with a distance of 13 cm between them, the temperature of the plasma medium similar to the thin film coating conditions was obtained with the Collisional Radiative Model. The spectrum was simulated using a collisional radiative model and plasma temperature was determined from line intensity ratio (Goktas, Demir, Kacar, Hegazy, Turan, Oke & Seyhan, 2007).

2. EXPERIMENTAL AND MODELING DETAILS

The Figure1 shows the vacuum plasma system. The vacuum chamber is made of stainless steel (Nanovak, NVPR500-01) with a diameter and height of 50 cm. In the center of the chamber, there are two parallel stainless-steel plates of 15 cm in diameter and 0,8 cm in thickness, with a distance of 13 cm between them. The pressure of the vacuum chamber can be pumped down to a maximum of 10^{-7} Torr base pressure by 15 m^3/h mechanical pumps and a 400 L/s turbo molecular pump (Nidec, EN-8T1). The gas is pumped into the vacuum chamber by a needle valve at a continuous dynamic gas flow in the range of $1 - 50$ sccm. A DC- Glow discharge is set up and operated by applying an electric potential difference under vacuum between the electrodes that are, anode (high potential) and a cathode (low potential).

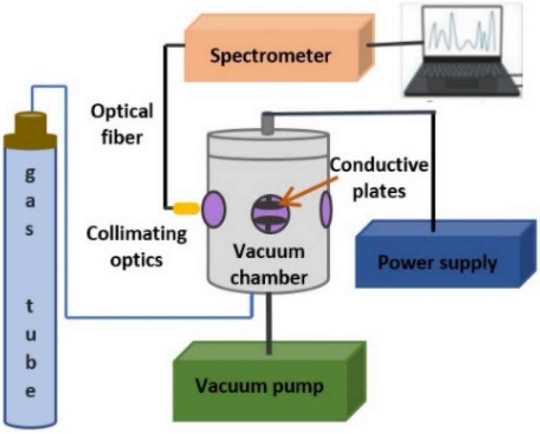

Figure1. Vacuum plasma system.

The free electrons are accelerated under applied potential within the neutral gas to the higher potential that ionizes the neutral gas particles along their path resulting in release of more electrons. The ions produced are accelerated towards the lower potential cathode, where they collide with the electrode acquiring an electron and colliding with the other electrons off the electrode into the plasma. Argon DC glow discharge plasma was produced in the vacuum chamber at 5 mTorr pressure, $24.6 - 24.9$ sccm gas flow, and 584 V potential difference applied between parallel plates (see Figure 1).

Radiation arises as a result of the interaction of electrons in the plasma with atoms or ions. In this case, three electron transitions can take place during these interactions: bonded-bonded transitions; unlimited passes; and free free passes. Light emitted from transitions creates line or continuous spectra. Atoms and ions of the gas and trace impurities emit radiation, which are in narrow spectral lines, when electron transitions occur between the various energy levels of the system (Garamoon, Samir, Elakshar, Nosair and Kotp, 2007).

According to the electron interaction process, McWhirter has suggested four plasma models, namely the local thermal equilibrium (LTE) model, the steady-state corona model, the time-dependent corona model, and the collision radiative model (P. McWhirter,1965).

Whether the plasma is in Local Thermal Equilibrium or not is determined by the McWhirter criteria (Adrain, 1982). The Mc Whirter Criteria can be expressed as,

$$n_e \gg 10^{19} \left(\frac{T}{e}\right)^{\frac{1}{2}} \left(\frac{\Delta E}{e}\right)^3 \left(\frac{1}{m}\right)^3 \tag{1}$$

where n_e electron density, T electron temperature, e electron charge ΔE energy difference. Accordingly, the electron density has to be greater than the McWhirter equation. If the electron density satisfies this condition, the degree of ionization of the plasma and the total ion density is calculated by the Saha equation. Saha equation can be expressed as,

$$\frac{n_e n_{i+1}}{n_i} = \frac{g_{i+1}}{g_i} \left[2 \frac{m^3}{h^3} \left(\frac{2\pi T}{m}\right)^{3/2} e^{-\chi_i / kT} \right] \tag{2}$$

n_i ion density, h Planck constant, k Boltzmann constant; χ_i ionation energy. And the excited level densities of the ions are calculated by the Boltzmann equation. Boltzmann equation can be expressed as,

$$N_i = N_T g_i e^{-E_i / kT} \tag{3}$$

N_i excited level density, N_T total density, g_i statistical weight.

In the Collisional Radiative Model, ion densities and excited level densities are calculated by including the collisional and radiative processes between all levels. It can be calculated in two different ways, time-dependent and time-independent (Cowan, 1981). Ion density and excited level density change with respect to time can be expressed as,

$$\frac{dn_i}{dt} = n_e\left\{n^{i-1}S^{i-1} + n^{i+1}\left[R_{rr}^{i+1} + n_e R_{cr}^{i+1} + R_{de}^{i+1}\right] - n^i\left[S^i + R_{rr}^i + n_e R_{cr}^i + R_{de}^i\right]\right\} \quad (4)$$

$$\frac{dn_m}{dt} = \sum_k \{n_k[n_e C_{km} + A_{km} + B_{km}u(\lambda_{km})] - n_m n_e(C_{mk} + B_{mk}u(\lambda_{km})\} + n_e\left\{n^{i-1}S^{i-1} - n_i S^i + n^{i+1}[R_{rr} + n_e R_{cr} + R_{de}]\right\} \quad (5)$$

S ionation rate, R_{rr} radiative recombination rate, R_{cr} collisional radiative recombination rate, R_{de} dielectronic recombination, C collisional excitation rate, A spontaneous emission rate, B stimulated emission rate, u energy density, λ wave length. In this study, the densities of the energy levels were calculated according to the plasma temperature and density using the Collisional Radiative Model (equations 4-5) in PrismSPECT software.

Coronal Equilibrium Model is used in low-density plasma conditions. In this model, the radiation processes dominate because the collision processes are very weak due to the low density of the plasma (Hutchinson, 2002). In Coronal Equilibrium Model, it is assumed that changes in energy levels result from radiative processes. Coronal Equilibrium model is valid under low density and high-temperature plasma conditions. Electron density condition for Coronal Equilibrium can be expressed as,

$$n_e < 5{,}6 \times 10^{14}(Z+1)^6 T_e^{\frac{1}{2}} exp\left[\frac{1{,}62 \times 10^3 (Z+1)^2}{T_e}\right] \quad (6)$$

where Z is atomic number.

3. RESULTS AND DISCUSSION

The spectrum of the Argon glow discharge plasma produced in the vacuum is presented in Figure 2. This spectrum was recorded by a high-resolution Optical Emission Spectrometer. Baki spectrometer is a Czerny-Turner type emission spectrometer between $200 - 1100\ nm$, with integration time min. $10\ \mu s$, resolution $0.5\ nm$, and trigger inputs and outputs. Since the plasma medium is continuous medium, measurements were made in $100\ ms$ without any delay on the spectrometer. The rays emitted from the plasma were collected with a $1 - inch$ focal length parabolic mirror (Thorlabs) and propagated to the spectrometer with a fiber optic cable. The experimental spectra were simulated using a collisional radiative plasma code PrismSPECT software. The simulated spectrum of Argon plasma at $T_e = 2\ eV$ and $\rho_e = 1 \times 10^{-4}\ gr/cm^3$ is shown in Figure 3.

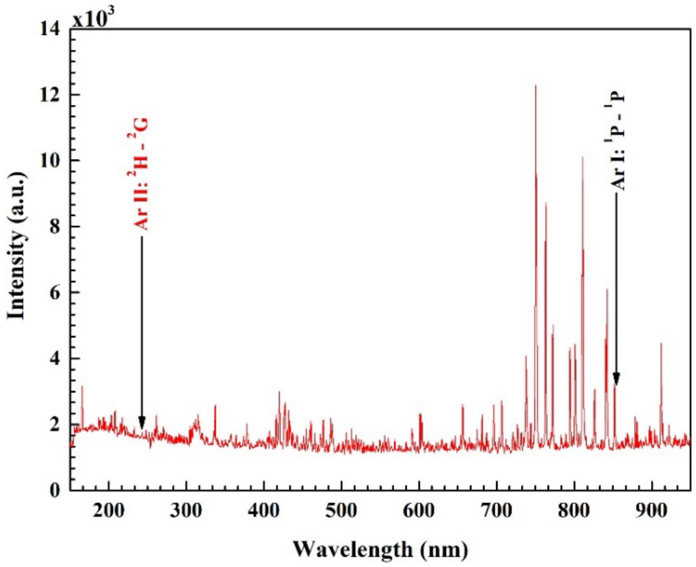

Figure 2. Optical Emission Spectrum of Argon glow discharge plasma produced in the laboratory.

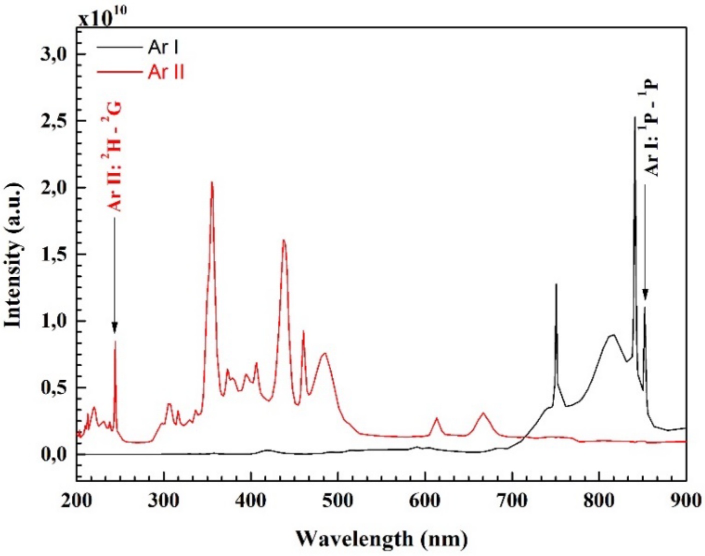

Figure 3. The simulated spectrum of Argon plasma at $T_e = 2\ eV$ and $\rho_e = 1 \times 10^{-4}\ gr/cm^3$ with the PrismSPECT collisional radiative code.

It is presented in Figure 2 that the second ionization line is at 244.4 nm and its intensity is 1.76 a.u, the first ionization line is at 852.5 nm and its intensity is 3.16 a.u. Since the densities of the excited levels of two different ions are more sensitive to the electron temperature, the excited levels of ArI and Ar II ions were chosen for temperature measurement. In experimental measurements, the signal-to-noise (SNR) ratio $(SNR = P_{signal}/P_{noise})$ decreases due to the noise in the CCD of the spectrometer, and ArII ion densities seem low. Cooling the CCD detector can be beneficial to reduce noise. In the simulated spectrum of Argon plasma, it is only seen the spectral lines of the first ionization and the second ionization of argon. Therefore, as there are different ionizations of argon gas there are more ionization spectral lines in the experimental spectrum. The experimental intensity ratio of the spectral line of the second ionization of argon to the spectral line of the first ionization of argon is $\mathrm{Ar_{II}}/\mathrm{Ar_{I}} = 1.76/3.16 = 0.556$.

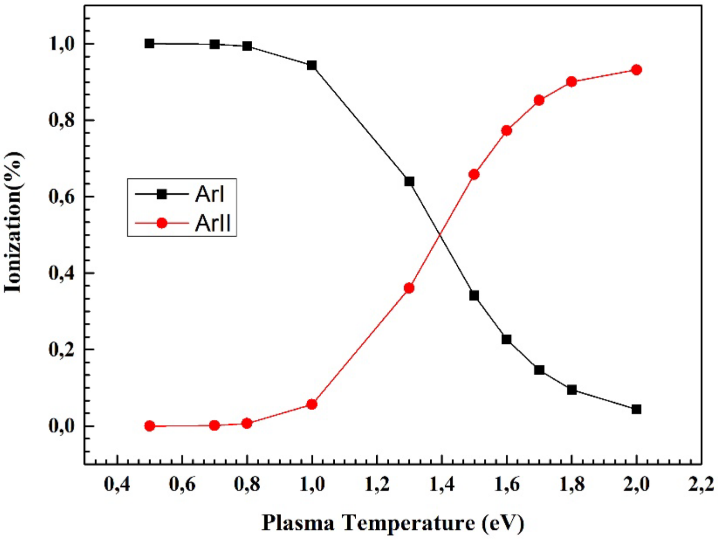

Figure 4. Graph of temperature versus percent ionization at a constant mass density of $\rho_e = 1 \times 10^{-4}\ gr/cm^3$.

Figure 4 shows the temperature versus the ionization percentage at constant mass density of $\rho_e = 1 \times 10^{-4}\ gr/cm^3$ with the PrismSPECT program. And Figure 5 shows simulated mass density versus the ionization percentage at the constant temperature of $\mathrm{T_e} = 2$ eV. As seen from Figure 4 while the temperature-dependent change of the first ionization percentage of argon decreases towards high temperature, temperature-dependent change in the second ionization percentage of it increases towards high temperatures. As illustrated in Figure 5, while in the mass density graph of the ionization percentage the mass density variation of the first ionization percentage of argon increases towards high mass density, the second ionization percentage of argon decreases towards high mass density.

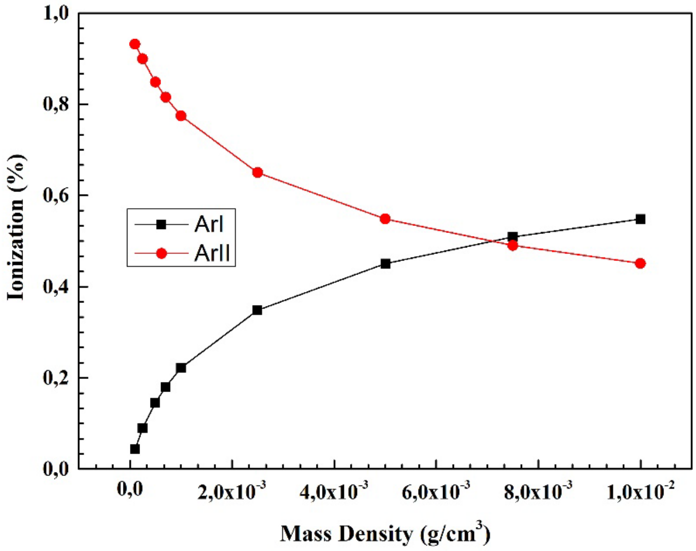

Figure 5. Graph of mass density versus percent ionization at a constant temperature of $T_e = 2$ eV.

The Figure 6 shows that a graph of the change of the ratio of the second ionization to the first ionization of argon versus mass density at a constant temperature of $T_e = 2\ eV$ in the simulated with the PrismSPECT program. And also Figure 7 shows the intensity ratio of the second ionization to the spectral line of the first ionization of argon versus temperature at a constant mass density of $\rho_e = 1 \times 10^{-4}\ gr/cm^3$. The atomic data taken from NIST (atomic-spectra-database) for the lines is shown in Table 1.

TABLE 1. Atomic data of Argon spectral lines.

Ion	**Upper configuration**	**Term**	**Lower configuration**	**Term**	**wl(nm)**	**Osc. Str.**
ArI	$1s^22s^22p^63s^23p^54p^1$	^1P	$1s^22s^22p^63s^23p^54s^1$	^1P	852.35	0.151
ArII	$1s^22s^22p^63s^23p^44f^1$	^2H	$1s^22s^22p^63s^23p^44d^1$	^2G	244.3	0.1979

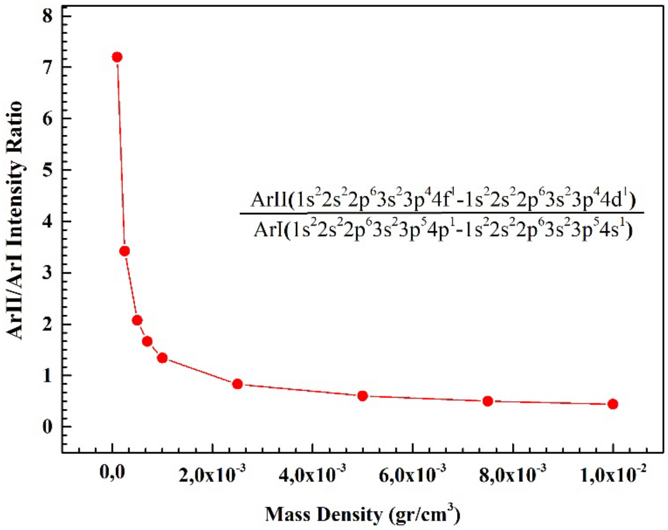

Figure 6. Graph of the change of the ratio of the second ionization to the first ionization of argon versus mass density at a constant temperature of $T_e = 2\ eV$.

As seen from Figure 6 and Figure 7, respectively, the intensity ratio of the spectral lines of argon decreases with respect to mass density, while the ratio of spectral lines of argon increases with respect to a higher temperature. The experimental intensity ratio of spectral lines ($\mathrm{Ar_{II}}/\mathrm{Ar_{I}} = 1.76/3.16 = 0.556$) obtained from Figure 2 is shown in the graph simulated by the PrismSPECT program in Figure 7. Accordingly, as seen from Figure 7 that the electron temperature of the Argon DC glow discharge plasma generated in a vacuum chamber is approximately **1.66 eV**

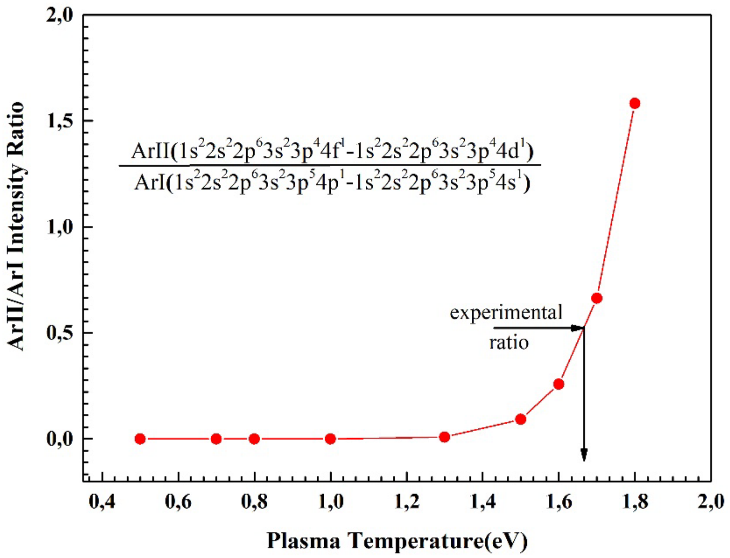

Figure 7. Graph of the change of the ratio of the second ionization to the first ionization of argon versus temperature at a constant mass density of $\rho_e = 1 \times 10^{-4}\ gr/cm^3$.

5. CONCLUSION

DC glow discharge Ar plasma was created under vacuum, and the photons emitted from the plasma were analyzed by optical emission spectrometry. The emitted spectrum of the argon plasma was simulated by the PrismSPECT program. Plasma temperature was obtained from spectrum line ratios. By comparing the spectrum of Argon DC glow discharge plasma taken with an optical emission spectrometer with simulation graphics of ArII/ArI emission intensity ratio calculated with the PrismSPECT program, the temperature of the plasma created in the vacuum environment is approximately shown. In this study, Argon plasma conditions used in thin-film coating environments were examined spectroscopically and it contributed to the understanding and interpretation of similar plasma environments by simulation.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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